— SECTION B —

CHEMICAL SCIENCES

Contents

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXIV. THE CYCLIC SULPHITES OF *meso*- AND *levo*-2,3-BUTANEDIOL[1]

BY FLORENCE M. ROBERTSON[2] AND A. C. NEISH[2]

Abstract

levo-2,3-Butanediol reacts spontaneously with thionyl chloride to give good yields of its cyclic sulphite (b.p. 177° to 178° C.). This ester is optically active ($[\alpha]_D^{25} = 19.9°$) and can be hydrolyzed by dilute hydrochloric acid to pure *levo*-2,3-butanediol and sulphurous acid. The cyclic sulphite of *meso*-2,3-butanediol (b.p. 188° to 189° C.) was also prepared.

Introduction

Thionyl chloride is frequently used for the replacement of a hydroxyl group by a chlorine atom (2, p. 84). In this laboratory it was used in an attempt to replace the hydroxyl groups of *levo*-2,3-butanediol, to form the chlorohydrin. Instead of the expected reaction, however, it was found that the cyclic sulphite of *levo*-2,3-butanediol formed as follows:
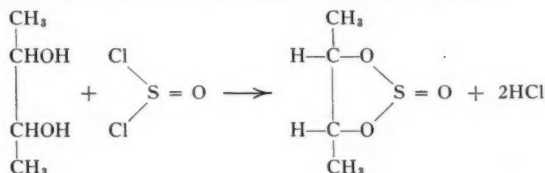
The ester thus obtained was optically active; on acid hydrolysis pure *levo*-2,3-butanediol was recovered, showing complete retention of configuration. *meso*-2,3-Butanediol also reacted with thionyl chloride to give an isomeric sulphite. The properties of these compounds are given in Table I. They are colourless liquids, immiscible with water, but easily hydrolyzed by acids and alkalis. The specific rotation of the *levo*-isomer is extremely sensitive to temperature changes, varying from +19.80° at 24.5° C. to +21.31° at 32° C. Because these compounds have a greater difference between their boiling points (11° C.) than any other known derivatives of the 2,3-butanediols, they might prove useful in the separation of *dextro*- or *levo*-2,3-butanediol from the *meso*-isomer.

A compound analogous to these was prepared by Schiller (9) from diethyl tartrate and thionyl chloride, and other workers have reported compounds of the type (RO)$_2$SO as reaction products of thionyl chloride with alcohols (3, 5, 8). Recently Kolfenbach *et al.* (4) have prepared a cyclic carbonate of 2,3-butanediol by reaction with phosgene. It is possible that this reaction is general when 2,3-butanediol is treated with acid chlorides.

TABLE I

PHYSICAL PROPERTIES OF THE CYCLIC SULPHITES OF 2,3-BUTANEDIOL

——	Sulphite of *levo*-2,3-butanediol	Sulphite of *meso*-2,3-butanediol
Boiling point, ° C.	177–178	188–189
Density, d_4^{25}	1.192	1.211
Refractive index, 25° C.	1.4296	1.4368
Specific rotation, $[\alpha]_D^{25}$	+ 19.92°	—

Experimental

Materials and Methods

levo-2,3-Butanediol, containing about 3% water, was obtained from the pilot plant fermentation of wheat by *Aerobacillus polymyxa* (6). The *meso*-isomer was prepared by the fractional distillation through a Stedman column of crude *meso-dextro* glycol obtained in the pilot plant from the fermentation of molasses by *Aerobacter aerogenes* (1). The purified material had an optical rotation of +0.20°. Eastman's practical grade thionyl chloride was used.

Carbon and hydrogen values were obtained from combustion of the compounds by Liebig's method, lead chromate and silver ribbon being added to the packing to remove sulphur.

To determine the sulphur, 200-mgm. samples of the compounds were refluxed with 15 ml. of 5 M nitric acid for half an hour; the sulphate thus formed was precipitated as barium sulphate and weighed according to the usual procedure. The ease with which the sulphur was oxidized was strong evidence for the proposed cyclic sulphite structure; few organic compounds yield their sulphur under such mild conditions.

The compounds decomposed slowly on standing and in every case the analyses were performed on freshly distilled material.

Cyclic Sulphite of meso-2,3-Butanediol

Thionyl chloride, 160 ml. (2.2 moles) was added dropwise to 180 ml. of *meso*-2,3-butanediol (2 moles) in a 1-litre, three-necked flask equipped with a dropping funnel, glycerol-sealed stirrer, and reflux condenser. The reaction mixture slowly turned dark brown. Although at first heat was evolved, later the reaction mixture spontaneously became cool, and after all the thionyl

chloride had been added, the temperature had dropped to $-1°$ C.* Stirring was continued and the flask was gradually heated to drive off as much hydrogen chloride gas as possible. The reaction mixture was distilled through a column of glass helices. A small amount of yellow material distilled over at a low temperature. The yield of the sulphite (collected from $182°$ to $189°$ C.) was about 212 gm. (78% yield). Calc.: C, 35.30; H, 5.88; S. 23.53%. Found: C, 35.44, 35.49; H, 6.03, 6.04; S, 23.70, 23.56%.

Cyclic Sulphite of levo-2,3-Butanediol

The *levo*-compound was prepared in the same way as the *meso*-compound. The yield of product collected from $170°$ to $178°$ C. was 190 gm. (70% yield). Calc.: C, 35.30; H, 5.88; S, 23.53%. Found: C, 35.23, 35.25; H, 5.80, 5.91; S, 23.44, 23.26%.

Hydrolysis of levo-2,3-Butanediol Cyclic Sulphite

Sixty-eight grams (0.5 moles) of the sulphite was heated with an equal volume of 0.5 N hydrochloric acid in a 500-ml., three-necked flask equipped with a stirrer, a reflux condenser, and a capillary. A stream of air was passed through the reaction mixture to carry off the liberated sulphur dioxide. After about four hours, when only a slight milkiness remained, the reaction mixture was neutralized to the phenolphthalein end point with 5 N sodium hydroxide solution, cooled, and filtered to remove sodium chloride crystals. The filtrate was extracted with ether in a continuous extractor for about 40 hr. Fractional distillation of the ether extract yielded 42.7 gm. of *levo*-2,3-butanediol. When allowance was made for the fact that only 97% of the diol was extracted in the apparatus used, the yield was 98%. The high optical rotation showed that the diol was the *levo*-isomer. The fraction from $176.5°$ to $177.0°$ C. had a rotation of $-12.62°$, and a later fraction boiling at $177.0°$ C., had a rotation of $-13.03°$ (6). The 2,3-butanediol was identified by preparation of the di-(p-nitrobenzoate) which melted from $143.0°$ to $143.5°$ C. (corr.), as did the authentic derivative and a mixture of the two. No evidence of any other isomer was found by crystallization, and the optical rotation of a 4% solution of the derivative in dioxane indicated that it was 99 to 100% pure *levo*-derivative (7).

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* *The authors are unable to explain this unusual behavior. The reaction appears to proceed in two stages, the first exothermic, and the second, endothermic.*

THE OXIDATION OF METHANE AT HIGH PRESSURES

IV. EXPERIMENTS USING PURE METHANE AND COPPER, SILVER, ZINC, NICKEL, OR MONEL METAL AS CATALYSTS[1]

BY E. H. BOOMER[2] AND S. N. NALDRETT[3]

Abstract

Mixtures of methane and oxygen with some nitrogen were passed over catalysts of copper, silver, zinc, nickel, and Monel metal and the yields of methanol and other liquid products determined. The conditions of temperature, pressure, and rate of flow that were known to be best for a copper catalyst were used. Nickel and Monel metal appear to offer most promise. A massive form of catalyst appears to be better than a catalyst in the form of fine wire gauze for the maximum yield of liquid products.

Introduction

The present report is a continuation of a systematic investigation of the oxidation of methane at high pressures. Boomer and Thomas (3) passed mixtures of natural gas (substantially methane) and air in various proportions over catalysts and determined the effects of the variables: composition of the gas mixture, pressure, temperature, and space velocity. Similar investigations were carried out using mixtures of pure methane containing some nitrogen, and oxygen (4). Copper was the principal catalyst used but a few observations were made using catalysts of glass, nickel-chromium steel, or silver. They concluded that the action of the catalyst is twofold: (1) to provide a surface easily oxidized and reduced, and (2) to aid in the dissipation of the heat of the reaction. They believed gas phase reaction and lack of temperature control to be detrimental to the survival of useful liquid products.

In the investigation described in the present paper, the optimum conditions as found for a copper catalyst by Boomer and Thomas (3, 4) were adopted. Various metals have been used as catalysts in an attempt to find the best catalyst for the production and survival of methanol.

Experimental

The experimental methods were substantially the same as those described in previous reports; some modifications were introduced and are described in what follows.

Materials

Natural gas from the Viking field near Edmonton was used. The composition of this gas, determined by ordinary combustion analysis, was approximately:

CH_4	90.8%
C_2H_6	3.5%
N_2	5.7%

Higher hydrocarbons such as propane were present in small amounts, and are included in the ethane figure. The gas had been artificially odorized with mercaptans and alkyl disulphides. The higher hydrocarbons and the sulphur compounds were pyrolyzed and the products of pyrolysis removed by a method that has been described (2). The composition of the gas produced was approximately 90% CH_4, 10% N_2; about 0.1 to 0.2% ethylene was still present. Analysis also indicated that the gas contained sulphur. The sulphur was apparently in an organic combination and was not absorbed in 40% potassium hydroxide solution, or by sodium hydroxide flakes, or by soda lime, or by triethanolamine. Ignition of the gas and absorption of the products of combustion in sodium carbonate solution as in a standard method of analysis (5) indicated a sulphur content of 0.3 to 0.5 grains per 100 cu. ft., which could not be reduced further by any amount of alkaline absorbents. Passing the gas through a condensing trap at about $-100°$ C. reduced the sulphur content to an undetectable amount. However, for the large quantities of gas required for the preliminary survey of catalysts it was not practicable to make this purification. In any case, it would be valuable to find a catalyst that can resist poisoning by sulphur. Therefore, for the series of experiments reported here, it must be borne in mind that the catalysts are not operating at their optimum, and that further improvements can undoubtedly be made.

Oxygen as required was added to the gas from a commercial cylinder and the gas mixture was then compressed and pumped into the high pressure storage tanks.

Catalysts were used in three forms: as cylindrical pieces $\frac{1}{4}$ in. long cut from wire 0.08 in. diameter; as blocks about 3/16 in. square and 3/32 in. thick, and in the form of gauze. The reactor (the same one described in earlier investigations (3)) was tubular in shape, with a smaller tube, the thermocouple well, entering one end and projecting halfway into the reactor. Rings of gauze were punched out of a sheet to fit snugly into the reactor and pass over the thermocouple well. These rings were packed into the reactor up to the level of the end of the thermocouple well; the remainder of the reactor was packed with gauze disks. The gauze used was about 60 mesh, the diameter of the wire being 0.006 in.

The blocks and the gauze were originally copper. To obtain other surfaces, the copper blocks, or the disks and rings punched from copper gauze, were electroplated with the desired metal. In the form of blocks, copper and nickel surfaces were investigated; in the form of gauze, copper, silver, nickel, and

zinc surfaces were examined.   Monel metal was investigated as cylindrical pieces cut from wire.

In the cases of the surfaces obtained by electroplating copper gauze, plating did not occur at the points where the wires crossed, and copper was left exposed. The inside of the reactor also was copper-plated in all experiments but the total surface of copper was nevertheless slight in comparison with the surface of the metal being investigated.

Apparatus

The reaction system and its operation were the same as have already been described in detail (1, 3, 4) except in one regard—whereas in the investigation described in the earlier papers the methane and oxygen were stored separately under high pressure and mixed under high pressure as required in the course of an experiment, in the present investigation oxygen was added to the methane before compression.   A single high pressure storage tank was used, and the pressure in the system was kept constant throughout an experiment by means of an automatic compression system as described earlier (4).

The catalyst was activated by alternate oxidation and reduction at the temperature at which the trial was to be made.   Air was used to oxidize the catalyst; hydrogen and methanol vapor were used as a reducing agent.

The collection of samples and the methods of analysis were the same as those reported by Boomer and Broughton (1).   As in the earlier investigations, the volume of in-gas was not measured directly, but was calculated from the measured amounts of off-gas and liquid products, using the element carbon as a reference.   On the basis of a carbon balance, oxygen appeared to be lost, a phenomenon that has been observed in other investigations and has not yet been explained (4, 6).

Results and Discussion

A comparison of the effect of the block form of copper with the gauze form is presented in Table I.   Experiments 1 to 5 with copper blocks were made under the same conditions as those for which Boomer and Thomas (4) obtained yields of about 60% methanol on the basis of percentage of carbon oxidized. The catalyst was reactivated after Experiment 2 in case the catalyst had become poisoned by oil contamination.   The yield of methanol was increased somewhat as shown by Experiments 3 to 5 but was still below that obtained by Boomer and Thomas, probably owing to the sulphur content of the gas. Reactivation of the gauze catalyst after Experiment 7 also gave some improvement in yield of methanol.   The yield appeared then to be steady in Experiments 8 to 10, but considerably below that obtained using copper blocks.   This was not expected since a copper surface was known to be beneficial, and in these trials the area of copper surface had been greatly increased.   However, the weight of copper used as catalyst in the form of gauze was only two-thirds the weight of the copper blocks.   Hence, there was more free space in the reaction system when gauze was used, and, therefore, more opportunity for detrimental gas phase reactions.   It is also probable

TABLE I

EXPERIMENTS COMPARING COPPER GAUZE AND COPPER BLOCKS

Experiment No.	1	2	3	4	5	6	7	8	9	10
Catalyst	Blocks	Blocks	Blocks	Blocks	Blocks	Gauze	Gauze	Gauze	Gauze	Gauze
Temperature, ° C.	450	450	450	450	450	450	450	450	450	450
Pressures, atm.	180	182	200	183	186	177	172	174	177	176
Off-gas flow, litres/min.	0.69	1.03	1.10	0.38	1.22	1.10	1.10	1.10	1.10	1.14
In-gas analysis:										
Olefins	0.45	0.45	0.45	0.45	0.40	0.22	0.22	0.11	0.11	0.17
O_2	5.5	5.6	5.8	5.8	5.7	6.3	6.0	6.0	6.1	5.7
CH_4	87.8	88.4	87.7	87.0	87.8	86.7	86.7	85.0	83.9	85.3
Off-gas analysis										
CO_2	1.25	1.20	1.30	1.55	1.30	1.72	1.84	1.60	1.50	1.50
Olefins	0.15	0.25	0.10	0.17	0.0	0.22	0.11	0.0	0.0	0.0
O_2	0.2	0.2	0.2	0.3	0.3	0.2	0.3	0.3	0.3	0.3
H_2	2.7	2.0	1.2	0.45	0.65	0.55	0.55	1.0	1.1	1.0
CO	1.5	1.5	0.65	0.2	0.4	0.90	0.45	0.7	0.7	0.6
C_2H_6	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	87.2	87.8	88.9	89.6	89.7	89.0	89.6	87.6	87.6	88.0
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.05	1.04	1.04	1.06	1.05	1.07	1.07	1.07	1.08	1.06
Condensate, gm./100 litres in-gas at N.T.P.										
Total	6.74	6.44	5.90	5.90	6.41	7.08	6.58	6.41	5.66	5.81
CH_3OH	1.80	1.90	1.85	1.74	1.84	1.02	1.02	1.33	1.32	1.15
CH_2O	0.033	0.022	0.025	0.042	0.035	0.086	0.086	0.048	0.048	0.049
HCOOH	0.044	0.032	0.028	0.024	0.031	0.022	0.026	0.033	0.031	0.034
H_2O	4.86	4.49	4.00	4.10	4.50	5.95	5.45	5.00	4.26	4.58
Alcohol in condensate, %	26.8	29.5	31.3	29.5	28.8	14.4	15.5	20.75	23.3	19.8
Total carbon oxidized, %	4.46	4.45	3.60	3.33	3.34	3.70	3.37	3.68	3.59	3.31
Yields, as % of total carbon burned to:										
CH_3OH	31.9	33.5	40.5	41.7	43.7	22.1	24.3	29.7	30.6	28.4
CH_2O	0.62	0.40	0.57	0.61	0.90	2.00	2.19	1.14	1.20	1.30
HCOOH	0.54	0.39	0.43	0.70	0.52	0.34	0.41	0.52	0.50	0.59
Total	33.06	34.29	41.50	43.01	45.12	24.44	26.90	31.36	32.30	30.29
Total inlet oxygen accounted for, %	106	99	83	87	91	100	100	96	81	93

that the surface temperature of the gauze was higher owing to the greater active area per unit mass of copper, and this decreased temperature control is probably responsible in part for the lower yields of methanol.

Table II gives the results of a series of experiments made to compare various metals as catalysts in the form of gauze. Experiments 11 to 13 using silver gauze gave less methanol than was obtained when copper gauze was used. Boomer and Broughton (1) and Boomer and Thomas (4) found silver to be

TABLE II

COMPARISON OF VARIOUS METALS IN THE FORM OF GAUZE

Experiment No.	11	12	13	14	15	16	17	18	19
Catalyst	Silver	Silver	Silver	Zinc	Zinc	Zinc	Nickel	Nickel	Nickel
Temperature, ° C.	450	450	450	450	450	450	450	450	450
Pressure, atm.	176	176	179	182	181	190	177	182	184
Off-gas flow, litres/min.	1.09	1.06	1.10	1.10	1.10	1.07	1.09	1.06	1.07
In-gas analysis:									
Olefins	0.17	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
O_2	5.8	5.9	5.9	5.8	5.8	5.8	5.8	5.8	5.8
CH_4	84.9	84.6	84.6	84.6	84.7	84.8	84.7	84.7	84.6
Off-gas analysis:									
CO_2	2.0	1.7	1.7	1.9	2.2	2.5	1.6	1.4	1.5
Olefins	0.0	0.05	0.1	0.05	0.05	0.05	0.05	0.07	0.05
O_2	0.2	0.25	0.3	0.3	0.3	0.3	0.3	0.25	0.3
H_2	0.65	2.2	2.4	3.0	2.6	3.0	1.7	1.6	1.7
CO	0.55	0.8	0.9	0.8	0.6	0.5	0.8	0.8	0.9
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	89.2	87.1	86.7	87.1	87.1	86.9	87.3	87.8	87.0
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.08	1.07	1.05	1.06	1.06	1.06	1.07	1.08	1.07
Condensate, gm./100 litres in-gas at N.T.P.									
Total	5.52	5.21	5.12	4.65	4.31	3.77	6.30	6.00	6.11
CH_3OH	1.01	0.96	0.90	0.70	0.57	0.06	1.54	1.55	1.49
CH_2O	0.032	0.043	0.037	0.009	0.013	0.009	0.018	0.017	0.018
HCOOH	0.036	0.036	0.029	0.032	0.031	0.003	0.043	0.042	0.040
H_2O	4.44	4.16	4.16	3.91	3.70	3.70	4.70	4.40	4.56
Alcohol in condensate, %	18.3	18.5	17.5	15.1	13.2	1.67	24.3	25.8	24.5
Total carbon oxidized, %	3.68	3.62	3.69	3.59	3.59	3.39	3.94	3.72	3.92
Yields as % of total carbon burned to:									
CH_3OH	22.5	22.0	20.0	16.1	13.0	1.53	32.1	34.3	31.4
CH_2O	0.76	1.05	0.88	0.23	0.32	0.24	0.40	0.41	0.40
HCOOH	0.56	0.57	0.45	0.51	0.50	0.43	0.64	0.65	0.59
Total	23.82	23.62	21.33	16.84	13.82	2.20	33.14	35.36	32.39
Total inlet oxygen accounted for, %	94	90	89	89	89	90	97	90	94

as good a catalyst as copper. However, in both of these previous investigations the form of the silver catalyst was not the same as the form of the copper catalyst with which it was compared. In view of the fact that the physical character of the catalyst appears to be important, the comparison of silver and copper in the previous investigations was probably not justified.

The low yields produced by the zinc gauze in Experiments 14 to 16 are not unexpected since reversible oxidation–reduction of zinc does not occur under

TABLE III

EXPERIMENTS WITH NICKEL IN THE FORM OF BLOCKS

Experiment No.	20	21	22	23	24	25	26
Temperature, ° C.	450	450	450	450	450	450	450
Pressure, atm.	185	188	182	181	185	179	181
Off-gas flow, litres/min.	1.07	1.07	1.09	1.10	1.09	1.18	1.07
In-gas analysis:							
Olefins	0.20	0.20	0.20	0.20	0.20	0.15	0.15
O_2	5.8	5.8	6.0	6.0	5.8	6.0	5.9
CH_4	84.6	84.7	84.0	85.0	85.1	84.4	84.6
Off-gas analysis:							
CO_2	1.15	1.3	1.5	1.7	1.7	1.1	1.15
Olefins	0.05	0.05	0.05	0.05	0.05	0.05	0.05
O_2	0.3	0.3	0.3	0.3	0.35	0.25	0.35
H_2	1.5	1.4	2.0	2.5	1.35	1.55	1.95
CO	1.2	1.1	0.90	0.80	0.60	1.25	0.90
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	87.5	87.6	87.2	86.7	87.4	86.7	87.4
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.07	1.07	1.07	.1.06	1.06	1.07	1.07
Condensate, gm./100 litres in-gas at N.T.P.							
Total	7.28	6.79	6.43	5.40	6.12	7.54	6.24
CH_3OH	1.76	1.70	1.49	1.36	1.42	1.76	1.41
CH_2O	0.062	0.053	0.032	0.036	0.027	0.056	0.032
HCOOH	0.033	0.030	0.029	0.033	0.028	0.027	0.030
H_2O	5.43	5.02	4.93	3.97	4.65	5.69	4.77
Alcohol in condensate, %	24.1	25.0	23.2	25.1	23.2	23.4	22.5
Total carbon oxidized, %	4.09	4.09	3.92	3.93	3.73	4.17	3.52
Yields as % of total carbon burned to:							
CH_3OH	35.3	34.1	31.6	28.3	31.1	34.9	32.9
CH_2O	1.34	1.14	0.68	0.79	0.64	1.19	0.80
HCOOH	0.46	0.42	0.43	0.47	0.42	0.37	0.48
Total	37.10	35.66	32.71	29.56	32.16	36.46	34.18
Total inlet oxygen accounted for, %	93	99	95	87	97	100	91

the conditions of these experiments and, consequently, the mechanism proposed for the production of methanol is not possible. These three experiments were made in sequence and it is suggested that during the first two experiments the oxidation of zinc was not complete but that late in the second experiment, or early in the third, the zinc had become completely oxidized and inactive, and hence almost no methanol was obtained in the third experiment.

Experiments 17, 18, and 19 offer a comparison of nickel, in the form of gauze, with the other catalysts. The yield of methanol is slightly higher than for copper gauze (Experiments 6 to 10) and appeared to be worth further study.

Catalysts should be compared under optimum conditions, differences in the behavior being most marked under the most favorable conditions; under unfavorable conditions all the catalysts may be expected to approach the same inefficient state. The results presented in Table I showed that gauze is not the best form of catalyst, at least for copper, and indicated that a comparison of the activities of various metals in the form of gauze should be considered only as a preliminary screening. Therefore, a series of tests was made with nickel in the form of blocks; the results are shown in Table III.

Comparing the two forms of each of the two catalysts, copper and nickel, the order of effectiveness is copper blocks (Table I), nickel blocks (Table III),

TABLE IV

EXPERIMENTS USING MONEL METAL

Experiment No.	27	28	29	30
Temperature, ° C.	450	450	450	450
Pressure, atm.	180	181	182	177
Off-gas flow, litres/min.	1.08	1.08	1.09	1.11
In-gas analysis:				
Olefins	0.15	0.17	0.15	0.15
O_2	5.8	6.0	6.1	6.1
CH_4	84.5	84.8	84.3	84.5
Off-gas analysis:				
CO_2	1.04	1.69	1.05	1.13
Olefins	0.05	0.05	0.05	0.05
O_2	0.35	0.45	0.35	0.35
H_2	1.55	1.7	1.95	2.08
CO	0.95	0.5	1.0	1.0
C_2H_6	0.0	0.0	0.0	0.0
CH_4	87.7	86.5	87.1	86.7
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.07	1.05	1.07	1.06
Condensate, gm./100 litres in-gas at N.T.P.				
Total	6.68	5.83	7.00	6.92
CH_3OH	1.57	0.98	1.58	1.57
CH_2O	0.027	0.017	0.032	0.033
HCOOH	0.031	0.024	0.035	0.025
H_2O	5.05	4.80	5.35	5.30
Alcohol in condensate, %	23.5	16.9	22.6	22.6
Total carbon oxidized, %	3.54	3.30	3.61	3.67
Yield as % of total carbon burned to:				
CH_3OH	36.7	24.5	36.2	35.3
CH_2O	0.67	0.46	0.78	0.80
HCOOH	0.50	0.42	0.56	0.39
Total	37.87	25.38	37.54	36.49
Total inlet oxygen accounted for, %	94	94	93	94

nickel gauze (Table II), and copper gauze (Table I). The two gauze catalysts gave very similar yields, suggesting that the form of the catalyst was the predominating influence in this case. When it is considered that the conditions of all of these experiments are those that have been determined to be the optimum for copper, nickel appears to offer some promise. It is possible that when the optimum conditions for the nickel catalyst have been determined it may show considerable superiority over copper.

It was also considered that the possible existence of a promoter effect might endow an alloy of copper and nickel with greater activity than is possessed by either metal alone. A series of experiments was therefore carried out using a catalyst of $\frac{1}{4}$ in. lengths of Monel metal wire 0.08 in. diameter. The results of Experiments 27 to 30 (Table (IV)) appear to demonstrate that Monel metal has catalytic properties quite similar to those of nickel. It may be somewhat superior to nickel, and in any case it also appears to be worthy of further study.

It is proposed that further experiments should now be carried out with both nickel and Monel metal. A systematic investigation of the effect of the variables, temperature, pressure, composition, and rate of flow is proposed, using sulphur-free gas, to determine the maximum conversion to methanol that can be obtained with these catalysts under the optimum conditions for each. It is expected that a considerable improvement in the conversion to methanol can be obtained by improving the conditions, following which consideration can be given to the advisability of investigating a recirculatory process.

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THE HETEROGENEITY OF ACTIVATED COCOANUT-SHELL CHARCOAL[1]

C. C. COFFIN[2] AND B. F. LONG[3]

Abstract

The individual adsorption capacities of over 500 granules of 6 to 10 mesh activated cocoanut-shell charcoal were determined by weighing each piece separately on a microbalance before and after saturation with carbon tetrachloride vapor. The particle capacities were found to be distributed over a probability curve represented by the equation

$$y = 14.6\, e^{-0.0036x^2}.$$

Small particles adsorb more carbon tetrachloride than large ones and dense particles more than those of lesser density.

Introduction

In the course of some work on the testing of activated cocoanut-shell charcoals for respirators, it was found that the observed activities seemed to depend on the method of sampling. This suggested that the material was heterogeneous in the sense that some particles were more adsorbent than others. In most of the work that has been done on such charcoals, relatively large samples containing many granules have been used. It is thus possible that significant differences in particle activity have been overlooked. This paper describes experiments designed to explore the extent and nature of any such heterogeneity. Attention is confined to the adsorption capacity (weight activity) of the dry charcoal.

Experimental

The individual adsorption capacities of the charcoal particles were determined by weighing each piece separately on a microbalance before and after saturation with carbon tetrachloride vapor. The torsion microbalance was adapted from that described in a paper by Fabergé (1). A sketch of its working parts is shown in Fig. 1. It was constructed from 'Meccano' parts firmly mounted in a strong wooden box. The torsion spring, T, consists of 104 turns (2 mm. in diam.) of 0.004 in. spring-tempered phosphor bronze wire. The ends of the spring are clamped in small brass chucks connected to the shafts, S and S', by standard Meccano couplings. The light glass beam, which is cemented to the middle of the helical spring, passes through a 2 by 1 mm. window in the side of the balance case into another closed chamber (a chalk box) provided with an easily operated and tightly fitting door of transparent plastic. The balance pan, P, is made of light aluminium foil and is

hung from the beam in this outer chamber in which an atmosphere of dry air or a partial pressure of carbon tetrachloride can be maintained. The end of the glass beam is drawn out into a fine point which, by moving the index, I, may be aligned with a similar fixed point and viewed through a lens system against an illuminated ground-glass background from the front of the balance. The adjustable pointer-index, I, is carried by the shaft, S, so that, by turning it counterclockwise, the spring may be wound up to offset the effect of a weight added to the pan. The dial is a 14 in. varnished cardboard protractor divided into 0.25 degrees of arc and mounted on a 'Masonite' panel. The sensitivity of the balance is 15.85° of arc per mgm. or 0.000016 gm. per scale division.
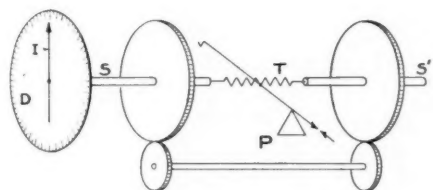

FIG. 1. *Working parts of microbalance.*

The geared construction does not limit the pointer movement to something less than 360° as is the case with Fabergé's instrument. It can be 'wound up' indefinitely. The calibration curve is strictly linear over the range used (5 to 25 mgm.) in the charcoal weighings. There is a hysteresis effect in that the zero point tends to drift slightly under load and return when the balance is at rest. This drift was checked and corrected for by determining the zero point after every fifth weighing. The balance is well damped and protected from drafts, and weighings can be made rapidly enough to avoid errors due to loss of carbon tetrachloride or pick-up of water vapor. By varying the length and diameter of wire and helix, a balance having practically any desired sensitivity can be very easily constructed.

To handle the individual pieces of charcoal, and to be able to identify them throughout a series of weighings, the following procedure was adopted. Arrays of narrow deep depressions in numbered rows and columns were stamped in square sheets of wire gauze to serve as receptacles for the charcoal pieces. Each gauze served as a tray that could be placed in oven (130°), desiccator, or carbon tetrachloride chamber. To carry out a series of measurements a piece of charcoal picked at random from a sample dried to constant weight was placed in each depression of a tray which was immediately put in a chamber at room temperature containing air saturated with carbon tetrachloride vapor. After coming to equilibrium, the particles were weighed as rapidly as possible and returned to their respective positions on the tray, which was then placed in the oven. After the carbon tetrachloride had been removed (16 hr. at 130° C.) the tray was placed in a shallow desiccator, the particles were weighed again, and the adsorption capacity of each piece was

calculated.   A shallow dish of carbon tetrachloride was placed in the balance
case during the first weighings and calcium chloride during the second.   No
difficulty due to loss of carbon tetrachloride or gain of water vapor was
experienced in obtaining a balance point.   Two operators are necessary
however—one to load and unload the pan, the other to balance it and record
the weights.

All experiments described here were made with a sample (SBT 95-96) of
charcoal obtained from the National Research Council.   In order to eliminate
any extreme differences in particle capacity that might be associated with very
large or very small particles, and in order to bring the pieces to be weighed into
a workable range on the balance, the sample was screened (unless otherwise
stated).   The fraction that passed a 6 mesh and was retained by a 10 mesh
screen was used for the measurements of individual adsorption capacity.

Results

The results obtained for 480 pieces of this 6 to 10 mesh charcoal are given
in Table I and are plotted as a distribution histogram in Fig. 2.   The amounts
of carbon tetrachloride taken up are tabulated and plotted in groups differing
by 5% based on the charcoal dry weight.   That is, the increment of the

TABLE I

DISTRIBUTION OF INDIVIDUAL ADSORPTION CAPACITIES

% CCl₄ adsorbed, (gm./100 gm. charcoal)	No. of pieces, (total = 480)	% of total No.
2	2	0.4
7	4	0.8
12	10	2.1
17	5	1.0
22	16	3.3
27	23	4.8
32	31	6.5
37	51	10.1
42	73	15.0
47	68	14.1
52	53	11.0
57	49	10.0
62	23	4.8
67	23	4.8
72	17	3.5
77	6	1.2
82	11	2.3
87	5	1.0
92	5	1.0
97	2	0.4
102	3	0.6

abscissa in the figure, and of Column 1 in the table, is 5%.   Thus, the ordinate at 27% adsorption, for example, gives the percentage of particles (Column 3) adsorbing between 25 and 29% inclusive of their dry weight of carbon tetrachloride.   The curve in the figure is the Gauss 'error' curve having an equation of the form

$$y = k \, e^{-h^2 x^2} \, ,$$

in which y is the ordinate of a point, k is a constant equal to the ordinate where $x = 0$, x is the positive or negative variation from this central ordinate, and h is a constant.   In the figure the constants ($k = 14.6$, $h = 0.06$) have been roughly fitted to the data in order to show that the type of heterogeneity found is that which might have been predicted for such a granular and randomly mixed material.   The point at which $x = 0$ has been taken as 47%.

$$y = 14.6 \, e^{-0.0036 x^2}$$

% TOTAL NUMBER OF PARTICLES

GRAMS OF CARBON TETRACHLORIDE ADSORBED
PER 100 GM. OF CHARCOAL
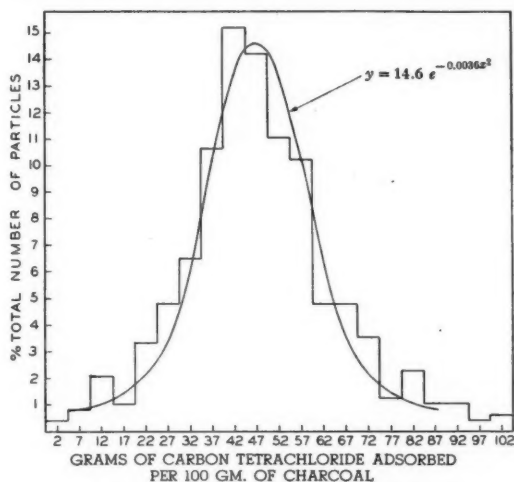
FIG. 2.   *Distribution of charcoal activity.*

The reproducibility of the method was tested by repeating the whole procedure with one lot (29 pieces) of charcoal.   The results are shown in Table II.   With few exceptions the two adsorptions agreed as closely as can be expected in work of this kind.

Charcoal Fractionation

The possibility of using some physical property to separate the charcoal into fractions of high and low adsorption capacity was investigated.   It was found that the smaller particles had a greater adsorption capacity and heat of wetting than the larger, and that the denser pieces had greater capacities than the less dense.

Figs. 3*A* and 3*B* show the distribution of adsorption capacity among manually separated large and small particles of 6 to 10 mesh charcoal.   Table III gives the relative heats of wetting (as temperature change per gram of

charcoal) in benzene of eight different 2 gm. batches of hand-separated large and small pieces.   It is evident that the smaller particles are more adsorbent than the larger.
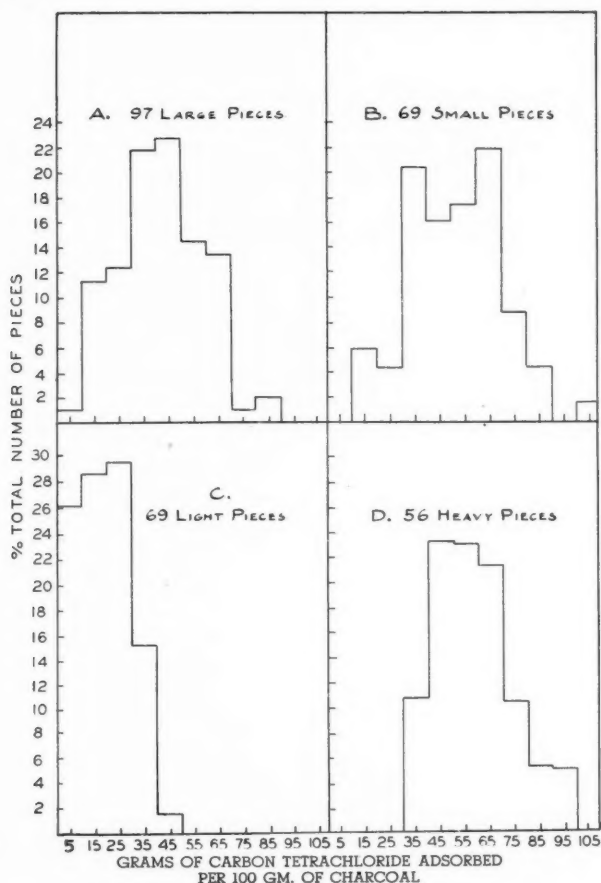
FIG. 3.   *Variation of charcoal capacity with size and density of particles.*

A more clean-cut separation of the charcoal into fractions of high and low adsorption capacity was achieved by fractional flotation in a liquid mixture. A dried 6 to 10 mesh sample was boiled in carbon tetrachloride to expel air. After cooling to room temperature the carbon tetrachloride (sp. gr., 1.6) and charcoal was stirred and slowly diluted with ethylene dibromide (sp. gr., 2.18) until about half the charcoal floated (sp. gr. liquid, 1.85).   The two charcoal fractions were then separated and, after removal of the carbon tetrachloride and ethylene dibromide, were investigated piece by piece on the microbalance.

TABLE II

RESULTS OF REPEATED DETERMINATION OF INDIVIDUAL ADSORPTION CAPACITY

Weights in milligrams

Weight dry piece		Weight saturated piece		Weight CCl$_4$ adsorbed		% Diff. CCl$_4$ weights
First	Second	First	Second	First	Second	
5.22	5.17	8.80	8.71	3.58	3.54	1.1
9.98	9.86	14.93	15.02	4.95	5.16	4.1
6.13	6.10	8.66	8.73	2.53	2.63	3.8
3.86	3.88	7.04	7.15	3.18	3.27	2.7
2.46	2.43	4.10	4.18	1.64	1.75	6.3
9.57	9.52	12.43	12.57	2.86	3.05	6.3
6.32	6.33	9.02	9.11	2.70	2.78	2.9
9.33	9.27	11.38	11.52	2.05	2.27	9.7
9.68	9.55	13.79	13.77	4.11	4.22	2.6
8.42	8.43	11.83	11.84	3.41	3.41	0
6.30	6.28	6.68	6.74	0.38	0.46	17.4
9.14	9.15	13.63	13.70	4.49	4.55	1.3
4.72	4.69	6.64	6.68	1.92	1.99	3.5
2.29	2.27	3.68	3.70	1.39	1.43	2.8
3.97	3.93	5.25	5.30	1.28	1.37	6.6
9.25	9.21	13.57	13.60	4.32	4.39	1.6
2.37	2.35	4.09	4.22	1.72	1.87	8.0
10.93	10.35	15.10	15.19	4.17	4.84	13.8
4.42	4.40	6.60	6.63	2.18	2.23	2.2
4.08	4.07	7.18	7.22	3.10	3.15	1.6
5.98	6.03	9.01	9.08	3.03	3.05	0.7
2.18	2.17	3.37	3.67	1.19	1.50	20.0
2.00	1.99	3.63	3.60	1.63	1.61	1.2
4.17	4.17	5.47	5.45	1.30	1.28	1.6
5.65	5.67	8.29	8.44	2.64	2.77	4.7
13.48	13.50	16.75	17.00	3.27	3.50	6.6
8.26	8.29	12.85	12.77	4.59	4.48	2.5
7.46	7.49	11.68	11.60	4.22	4.11	2.7
10.78	10.82	16.13	16.04	5.35	5.12	4.5

TABLE III

TEMPERATURE RISE IN BENZENE (20 CC. BENZENE; 2 GM. CHARCOAL; 20° C.)

Large pieces, ° C. per gm. charcoal	Small pieces, ° C. per gm. charcoal
2.07	2.65
2.02	2.44
2.13	2.38
2.05	2.44

The distribution of particle adsorption capacities in the light and heavy fractions is shown in Figs. 3C and 3D. It is evident that a remarkably sharp separation has taken place. This fractionation can be continued and small samples of very good and very poor charcoal may be readily obtained.

The writers are not aware of any previous work on this charcoal hetero-geneity, and are not prepared to discuss why some granules should be so much better than others.   The fact that small dense pieces are better than larger and lighter ones would seem, however, to point to differences existing among the cocoanut shells themselves rather than to 'ups and downs' in whatever activating process they have undergone.   Preliminary work has indicated that the best pieces of cocoanut charcoal are better than the best pieces of several synthetic charcoals, which, as might be expected, seem to be more uniform than the 'natural' variety.

A possibility that suggests itself here is the use of the probability equation, $y = k\,e^{-h^2 z^2}$, to describe charcoals or granular adsorbents in general.   Each specimen would be characterized by two constants, h and k, indicating its over-all adsorption capacity and the spread of the capacities of the individual particles.

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STUDIES IN THE FORMATION OF DDT[1]

BY T. A. EASTWOOD,[2] D. L. GARMAISE,[3] D. J. MORANTZ,[4] AND C. A. WINKLER[5]

Abstract

In the condensation of chloral and chlorobenzene in sulphuric acid to yield DDT, the yield of DDT is increased and the rate of formation of DDT decreased by (1) decreased sulphuric acid concentration, (2) decreased molar amount of sulphuric acid, and (3) lowered temperatures. Reversible sulphonation of chlorobenzene is the major side reaction; the presence of 4-chlorobenzene-sulphonic acid reduces the extent of this reaction. Increased yields (based on chloral) can be obtained by using excess chlorobenzene. A mechanism is proposed involving 1-(4-chlorophenyl)-2,2,2-trichloroethanol, which has been isolated from the reaction, and 1-(4-chlorophenyl)-2,2,2-tricholorethyl bisulphate, whose barium salt reacts with chlorobenzene in sulphuric acid to give DDT.

Introduction

The general reaction involving the condensation of two moles of an aromatic compound with one mole of an aldehyde to form a 1,1-diaryl alkane was first studied by Baeyer in 1872 (1) and has come to be known as the Baeyer condensation. It has recently been found that 1,1-di(4-chlorophenyl)-2,2,2-trichloroethane (p,p'-DDT), a product of this type of reaction first prepared by Zeidler (14), is a powerful contact insecticide (10).

In their research on the Baeyer condensation of chloral and benzene with sulphuric acid, Chattaway and Muir (4) were able to isolate 1-phenyl-2,2,2-trichloroethanol. Since this compound will react with one mole of benzene to give the normal Baeyer condensation product, they believe that this alcohol is a precursor of the usual Baeyer product. Previously, Dinesmann (6) had isolated the same alcohol using aluminium chloride catalyst, although neither he nor Frankforter and Kritchevsky (7) (who repeated Dinesmann's procedure) appear to have considered its intermediary nature. Rueggeberg et al. (12, 13) have reported the use of chlorosulphonic acid as the condensing agent and have postulated a mechanism for the reaction involving the alcohol as an intermediate. Mosher et al. (11) have reported their work on the preparation of technical DDT. Although their experimental techniques differ from those used in the present study, the conclusions they reach concerning the effect of the reaction variables are in qualitative agreement with those presented here.

The present study was initiated to determine the optimum conditions for the production of p,p'-DDT using sulphuric acid catalysis, and to investigate the mechanism of the reaction.

Experimental and Results

Materials

Chloral hydrate, Eastman's white label grade, was recrystallized once from chloroform.

Chloral, obtained by the dehydration of chloral hydrate with sulphuric acid, was purified by distillation. The product so obtained gave a negligible precipitate of aluminium hydroxide when refluxed with a toluene solution of aluminium isopropoxide, hence it was considered sufficiently anhydrous for the present purpose.

Chlorobenzene, Eastman's yellow label grade, was distilled and the fraction boiling between 131° and 132° C. was used.

Sulphuric acid, Baker's C.P. grade, was suitably diluted with distilled water, or fortified with Mallinckrodt's fuming sulphuric acid (25% SO_3) to give the desired strength. It was analyzed by titration with standard sodium hydroxide solution, which in turn was standardized with potassium hydrogen phthalate.

1-(4-Chlorophenyl)-2,2,2-trichloroethanol was synthesized by a method suggested by Barry (2). 4-Chloroacetophenone, formed from chlorobenzene and acetic anhydride with aluminium chloride catalysis, was photochemically chlorinated at 200° to 210° C. and the 1-(4-chlorophenyl)-2,2,2-trichloro-ethanone formed was reduced to the alcohol using aluminium isopropoxide. The white crystalline product melted at 47° to 47.5° C. (corr.) after several recrystallizations. It was further characterized by conversion to the acetate by Howard's method (9). The yield was 90% of the theoretical, the melting point of the product being 123° to 124° C. (corr.) (Howard reports 121° to 122° C.).

4-Chlorobenzenesulphonic acid was prepared according to the directions of Baxter and Chattaway (3). After one recrystallization from water it analyzed 94% pure and melted between 90° and 95° C.

Experimental Procedure

The desired amount of chloral hydrate was weighed (or if chloral itself, was measured from a microburette) into a tared 50 ml. wide-mouthed Erlenmeyer flask and the sulphuric acid added from a 50 ml. burette. The acid concentrations in the treatment which follows have been corrected for the dilution of the acid by the water content of the chloral hydrate. The chlorobenzene was then added to the reaction mixture as rapidly as possible from a 10 ml. burette. The flasks were clamped in a thermostat regulated within 0.1° C., each mixture being agitated by means of a glass stirrer of the centrifugal type, driven at about 600 r.p.m. from a countershaft. With certain mole ratios of reactants this type of stirring did not adequately agitate the dense DDT slurry produced; therefore in these experiments a ½ by 5 in. test tube replaced the usual 50 ml. reaction flask, and a closely fitting, flat twisted glass blade impeller was used.

The reaction was assumed to start when stirring was begun in the heterogeneous reaction mixture, and was quenched by diluting the sulphuric acid with about 20 gm. of chopped ice. About 15 ml. of chloroform was then added to the mixture to dissolve the organic material, and the acid layer carefully separated. The chloroform solution was then washed free of acid with distilled water, after which the chloroform and the small amount of water remaining were removed by distillation on a steam bath followed by heating for two hours at 50° C. at 1 mm. of mercury pressure. The net increase in weight was taken as crude DDT.

The p,p'-DDT content of the crude product was estimated by quantitative recrystallization from ethanol previously saturated with p,p'-DDT at 0° C. The procedure was adapted from that of the Chemical Inspection Department of the British Ministry of Supply as suggested by Messrs. Geigy (5). For each gram of crude product obtained, 10 ml. of solvent was added, and the solid was dissolved by heating the mixture under reflux. The p,p'-DDT was allowed to crystallize out by cooling the flask at room temperature for one hour and adding seeds if necessary. The crystallization process was continued at 0° C. for four hours. The precipitated material was filtered on a tared sintered glass crucible, washed twice with 10 ml. of cold 95% ethanol saturated with p,p'-DDT, dried to constant weight at 80° C., and weighed. For purposes of calculation the recrystallized material was assumed to represent all the p,p'-DDT in the sample.

The magnitude of the error involved in this method was estimated by analysis of synthetic mixtures of p,p'-DDT and o,p'-DDT. The main error is introduced by washing the chloroform solution with water, the accuracy of the entire procedure being about 5%. This was considered adequate in view of the nature of the reaction as a whole.

Stirring Speed and Rate of Reaction

Since the reaction is heterogeneous and the reactants form two layers, the effect of stirring speed was investigated. Two experiments were made using chloral, chlorobenzene, and sulphuric acid (97.4%) in a molar ratio of 1: 2: 20 at 30° C., one at stirring speed of 600 r.p.m. and the other at 1100 r.p.m. Since the rate of production was identical at both stirring speeds, subsequent experiments were made with a stirring speed of 600 r.p.m.

FACTORS AFFECTING THE YIELD OF DDT AND THE REACTION RATE

The effect of varying the acid concentration on the yield of DDT was investigated under widely different conditions of temperature and molar ratio of reactants, and by graphical interpolation of these data the yields of crude DDT for given acid concentrations and amounts shown in Table I were obtained. Since the general shape of the yield – acid concentration or

TABLE I

EFFECT OF ACID CONCENTRATION AND AMOUNT ON THE YIELD OF CRUDE DDT
AND TIME FOR COMPLETE REACTION

Acid concentration, %	Yield of crude DDT and reaction time with molar ratios of:													
	1:2:2		1:2:3		1:2:5		1:2:10		1:2:20		1:2:40		1:2:80	
	%	Hr.	%	Hr.	%	Hr.	%	Hr.	%	Hr.	%	Hr.	%	Hr.
0° C.														
97									73.5	21				
98									84.5	13				
99									82.3	8				
101									58.9	2				
30° C.														
93									77.1	120	66.5	36		
94									77.7	30	69.0	19		
95									77.8	14	70.0	9	60.4	3
96					69.7	68			76.0	7	68.0	4	58.4	3
97					80.5	42			73.8	3	63.0	2	55.8	2
98			77.0	190+	84.0	24			70.0	1	54.5	1		
99			83.2	140	81.8	13			64.0	$\frac{1}{2}$	42.5	$\frac{1}{2}$		
100			82.5	55	77.5	8			55.0	$\frac{1}{2}$	26.5	$<\frac{1}{2}$		
101			73.6	25	70.6	4			41.5	$<\frac{1}{4}$				
102			63.1	10	64.0	2			20.0	$<\frac{1}{4}$				
50° C.														
94					67.0	83	62.9	16						
96			60.0	70	71.9	27	67.5	6	60.4	2				
98			69.0	36	70.5	12	63.5	2	55.0	1				
100			73.0	24	65.3	5	50.0	$\frac{1}{2}$	39.9	$\frac{1}{2}$				
101	63.1	72+	72.7	21	61.7	3	39.0	$\frac{1}{4}$	26.5	$<\frac{1}{4}$				
102	63.5	72+	70.0	19					15.9	$<\frac{1}{4}$				
70° C.														
Maximum yield of p,p'-DDT														
94			15.0	18	21.0	10	23.2	5						
96			24.4	15	22.2	5	21.6	2						
98			25.8	12	22.8	3	19.9	$\frac{1}{2}$						
100	23.5	15	26.0	10	23.0	1	16.7	$\frac{1}{4}$						

yield – acid amount curves is not affected by temperature over the range
studied, only the values at 50° C., which are typical, are shown in Fig. 1
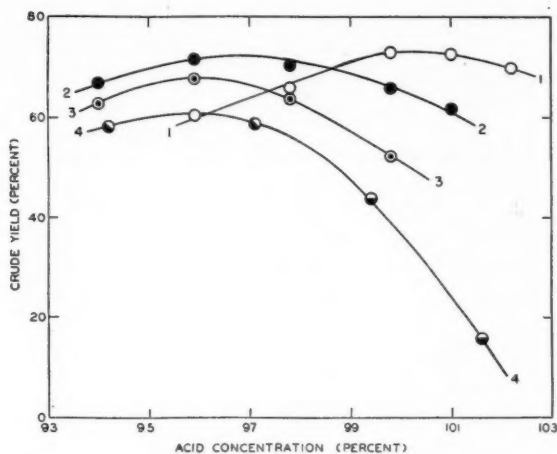(where the experimentally observed values are also plotted) and Fig. 2.

FIG. 1. *Effect of acid concentration on yield of crude DDT at 50° C. with chloral, chloro-benzene, and sulphuric acid in a molar ratio of 1 : 2 : 3—1; 1 : 2 : 5—2; 1 : 2 : 10—3; 1 : 2 : 20—4.*
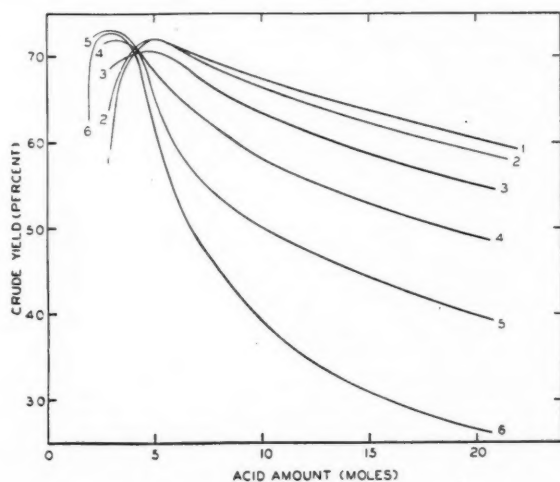

FIG. 2. *Effect of acid amount on yield of crude DDT at 50° C. with acid concentration of 96%—1; 97%—2; 98%—3; 99%—4; 100%—5; and 101%—6.*

Effect of Reactant Amounts

Experiments were made at 30° C. using other than the stoichiometric amounts of chlorobenzene, with the molar ratio of chloral to sulphuric acid maintained at 1 : 20.   The rate data are plotted in Fig. 3.
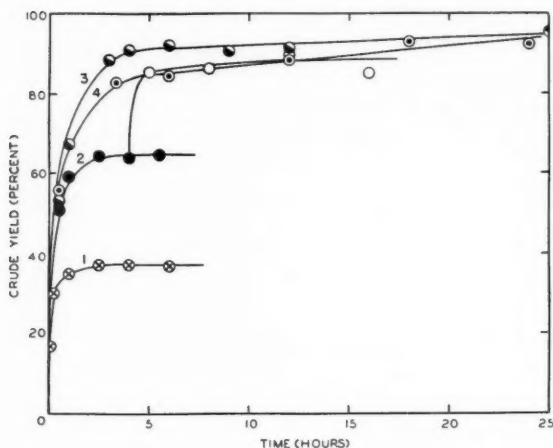
FIG. 3.   DDT formation with varying amounts of chlorobenzene at 30° C.   Chloral, chlorobenzene, and sulphuric acid in molar ratio of 1 : 1 : 20—1; 1 : 2 : 20—2; 1 : 4 : 20—3; 1 : 6 : 20—4.

Similar experiments were made with varying chloral amounts while the chlorobenzene – sulphuric acid ratio was 2 : 20. The results (Table II) indicate that, as compared with chlorobenzene, the chloral has little effect on the yield of p,p'-DDT.

When excess chlorobenzene was added to a normal reaction after the final yield of DDT had been reached, it was found that additional DDT was produced.   For example, if two moles of chlorobenzene be added to a normal reaction at the end of four hours the yield was increased from 64 to 89% (Fig. 3).

Similar results were observed when additional sulphuric acid was added to a normal reaction using small amounts of acid.   Using chloral, chlorobenzene, and sulphuric acid (101.9%) in a molar ratio of 1 : 2 : 3 for example, a yield of 64.4% was achieved in four hours and did not appreciably increase thereafter.   But if an additional 17 moles of acid (94.8%) be added at the end of this period the yield is increased to 74%, which is as great as if 20 moles of sulphuric acid (94.8%) had been present initially.   Presumably the catalytic action of the sulphuric acid had been inhibited by its dilution with the water formed from the DDT reaction and the sulphonation of chlorobenzene.

These results indicate that chloral or some compound intermediate between chloral and DDT is more stable in concentrated sulphuric acid than is chlorobenzene, and that the low yields obtained when the stoichiometric amount of chlorobenzene is employed are due to a side reaction involving chlorobenzene. Since 4-chlorobenzenesulphonic acid has been isolated from the acid layer at the end of a DDT reaction, and in view of the work of Mosher et al. (11), there can be little doubt that a major side reaction involved is the sulphonation of chlorobenzene.

TABLE II

DDT FORMATION WITH VARYING AMOUNTS OF CHLORAL AT 30° C.

Chloral, moles	Chlorobenzene, moles	Sulphuric acid (98.5%), moles	Time, hr.	p,p'-DDT yield, gm.	p,p'-DDT yield, %
0.0095	0.0191	0.191	0.25	0.68	20.0
0.01	0.02	0.20	0.50	1.16	32.8
			1.0	1.32	37.3
(Molar ratio 1 : 2 : 20)			2.0	1.40	39.3
			2.5	1.50	42.3
			4.0	1.59	45.0
			4.0	1.47	41.5
0.0191	0.0191	0.191	0.266	1.15	34.2
0.02	0.02	0.20	0.5	1.72	48.6
			1.0	1.73	48.9
(Molar ratio 2 : 2 : 20)			2.5	1.78	50.1
			4.0	1.87	52.7
0.0382	0.0191	0.191	0.25	0.90	26.9
0.04	0.02	0.20	0.5	1.79	50.5
			2.5	1.85	52.4
(Molar ratio 4 : 2 : 20)			4.0	1.89	53.4
			5.0	1.90	53.6
0.0572	0.0191	0.191	0.25	0.73	21.7
0.06	0.02	0.20	0.5	1.53	43.3
			3.0	1.60	45.5
(Molar ratio 6 : 2 : 20)			5.0	1.73	49.0

TABLE III

EFFECT OF ADDED 4-CHLOROBENZENESULPHONIC ACID ON DDT FORMATION

Chloral	0.01 mole (0.98 ml.)
Chlorobenzene	0.02 mole (2.04 ml.)
Sulphuric acid	0.20 mole (10.83 ml.)

Temperature, 30° C.

1	2	3	4	5	6
Added sulphonic acid, moles	Final crude yield,%	Final pure yield, %	Purity, %	Time for complete reaction, hr.	Concentration of H_2SO_4 allowing for sulphonic acid dilution, %
Nil	64.3	42.9	66.7	2.5	98.5
0.01	73.7	49.8	67.7	3.0	89.8
0.03	81.6	58.9	72.2	10.0	76.5
0.045	73.1	54.3	74.2	21.0	68.6
0.06	49.1	30.6	62.3	36.0	63.4

The shape of the yield – acid concentration or the yield – acid amount curves can then be explained on the basis of these two factors, the side reaction involving chlorobenzene, and the dilution of the catalyst. At low acid concentrations or amounts, the yields are low owing to the excessive dilution of

the catalyst so that further reaction to form DDT is immeasurably slow.   At higher concentrations or amounts this factor is not as important, and over a small range of concentrations the yield is maximal, representing optimum concentrations for a particular amount of acid at that temperature.   If the acid concentration or amount is further increased, the sulphonation reaction becomes more prominent than the DDT reaction and the yield decreases because of the inadequate supply of chlorobenzene.

Since the sulphonation of chlorobenzene is a reversible reaction the presence of the product should favor increased chlorobenzene concentrations and hence DDT yields; the truth of this surmise is indicated by the data in Columns 1, 2, and 3 in Table III.

Factors Affecting Reaction Time and Rate

The effect on the time necessary for complete reaction of varying the amount of chloral and chlorobenzene is clear from Table II and Fig. 3; chloral has little effect but an increase in the amount of chlorobenzene results in a longer reaction time.   This may be due to the greater dilution of the sulphuric acid by the water formed during the sulphonation of the chlorobenzene.

The minimum times required for the attainment of the final yield of DDT under different conditions of acid amount, concentration, and temperature have been given with the yields in Table I; those at 50° C. are typical in general outline and are shown in Fig. 4.   Evidently an increase in acid amount while the concentration is constant, or an increase in the acid concentration while the amount is constant, results in shorter reaction times.   Also, comparison of the results at different temperatures while the acid–reactant ratio is constant shows that an increase in reaction temperature results in a shorter reaction time, if the acid concentrations and amounts are fixed.
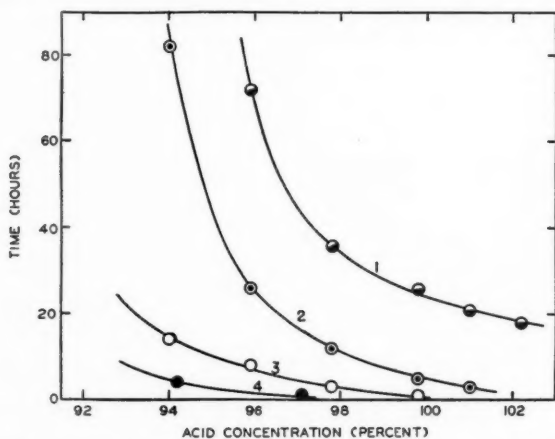

FIG. 4.   *Effect of acid concentration on time for complete reaction at 50° C. with chloral, chlorobenzene, and sulphuric acid in molar ratio of 1 : 2 : 3—1; 1 : 2 : 5—2; 1 : 2 : 10—3; 1 : 2 : 20—4.*

These curves show the high order of dependence on acid concentration and amount of the time for complete reaction. The shape of the curve for a molar ratio of 1 : 2 : 5 at 50° C., for example, shows the impracticability of working with acid concentrations below 94% under these conditions.

Not only does the time for complete reaction vary with the amount and concentration of the acid employed, but the velocity of the reaction also depends on these factors. Figs. 5 and 6 show typical rate curves for the production of DDT. In Fig. 5 the acid amount is varied while the concentra-
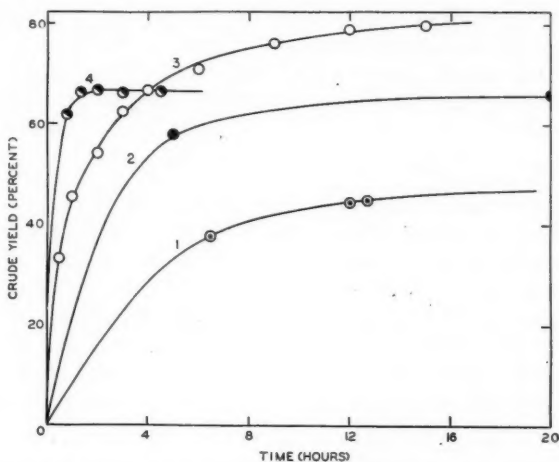

FIG. 5. *Effect of acid amount on rate at 30° C. with chloral, chlorobenzene, and sulphuric acid in molar ratio of 1 : 2 : 2—1; 1 : 2 : 3—2; 1 : 2 : 5—3; 1 : 2 : 10—4.*
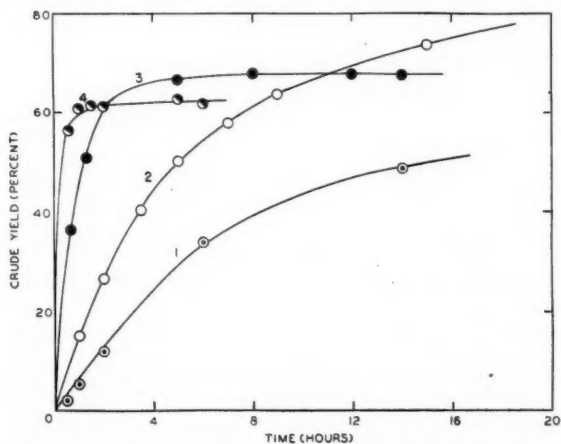

FIG. 6. *Effect of acid concentration on rate at 30° C. 93.1%—1; 94.3%—2; 98.3%—3; 99.4%—4.*

tion is constant, and in Fig. 6 the concentration is varied while the amount is constant. Since it is impossible to compare the rate curves using 93.1 and 99.4% or 2 and 10 moles of sulphuric acid on the same scale, only the early portions of the rate curves for low acid concentrations or amounts are shown graphically.

It is clear that an increase in acid concentration has the same qualitative effect as an increase in acid amount, namely, to increase the reaction rate.

Satisfactory specific rate constants for the reaction were not obtained, owing to the complexity of the main and side reaction, the experimental error, and the continual dilution of the sulphuric acid by the water eliminated in both the normal DDT reaction and the sulphonation of chlorobenzene. Initial rate measurements were also not sufficiently accurate to yield reliable rate constants.

Purity of the Crude Product

The formation of DDT isomers is a side reaction of equal importance with the sulphonation of chlorobenzene. The proportion of p,p'-DDT in the crude product (% purity of the product) has been found to be constant throughout a reaction under given conditions. The careful analysis of a number of samples of crude DDT from commercial sources has shown that the major impurity in crude DDT is 1-(4-chlorophenyl)-1-(2-chlorophenyl)-2,2,2-tri-chloroethane (o,p'-DDT) and that all other impurities together constitute less than 5% of the crude, depending on the purity of the initial reactants (8).

The p,p'-DDT: o,p'-DDT ratio is increased by decreasing the temperature, as shown by the average of all the purity values at a given temperature listed in Table IV.

TABLE IV

Effect of temperature on purity

Temperature, ° C.	Average purity, %
0	73.2
30	64.0
50	57.6
70	48.0

As shown by the values listed in Columns 1 and 4 of Table III the addition of 4-chlorobenzenesulphonic acid changes the ratio of the isomers. This may be because the 4-chlorobenzenesulphonic acid alters the reaction environment.

However, under three special conditions the purity of the product has not been found constant throughout the reaction.

(1). At 70° C. the purity decreases as the reaction time increases. The values given for the crude yield, p,p'-DDT yield, and purity of the crude product given in Table V are typical and indicate that some reaction is follow-

ing the formation of DDT by which the p,p'-DDT is being converted to a water insoluble, but alcohol soluble compound. Since the yield of the crude increases, the product formed cannot be a degradation product of p,p'-DDT, but may be a complex formed by polymerization or by reaction with sulphuric acid. For this reason only the maximum p,p-'DDT yield has been entered in Table I at 70° C.

TABLE V

CHANGE IN p,p'-DDT CONTENT OF CRUDE PRODUCT WITH REACTION TIME AT 70° C.

Chloral	0.02 mole (1.96 ml.)
Chlorobenzene	0.04 mole (4.07 ml.)
Sulphuric acid (96.1%)	0.10 mole (5.55 ml.)

Molar ratio 1 : 2 : 5

Time, hr.	Crude yield as % DDT	p,p'-DDT yield, %	Purity, %
1.0	29.7	14.8	49.8
2.0	35.4	18.2	51.6
4.0	52.2	22.6	43.3
9.5	55.2	21.6	38.4
20.0	57.6	19.8	34.4
28.0	61.8	—	—
36.5	62.7	18.2	29.0

(2). When excess chloral is used under otherwise normal conditions, the purity of the product is low. The impurity may be 1-(4-chlorophenyl)-2,2,2-trichloroethanol, since Chattaway and Muir have used somewhat similar conditions (i.e., excess aldehyde) to prepare the analogous compound, 1-phenyl-2,2,2-trichloroethanol (4). Since this may contaminate the crude product, only the p,p'-DDT yield was considered when the effect of excess chloral on the reaction was discussed.

(3). At 0° C., when the acid concentration was below 98.5%, it was found that the purity increased gradually to the value 73.2% previously established as the purity at 0° C.

The amount of impurity appearing in the early portions of the reaction can be calculated since the p,p'-DDT:total DDT ratio has previously been established as 73.2% at 0° C. From this ratio the total DDT yield for a corresponding p,p'-DDT yield can be arrived at, and the difference between the crude yield and total DDT yield represents the amount of impurity. By this method the values plotted in Fig. 7 were obtained. Since the impurity follows the appearance–disappearance curve usually associated with a reaction occurring in consecutive steps with about the same rates, the isolation and characterization of this material was undertaken.
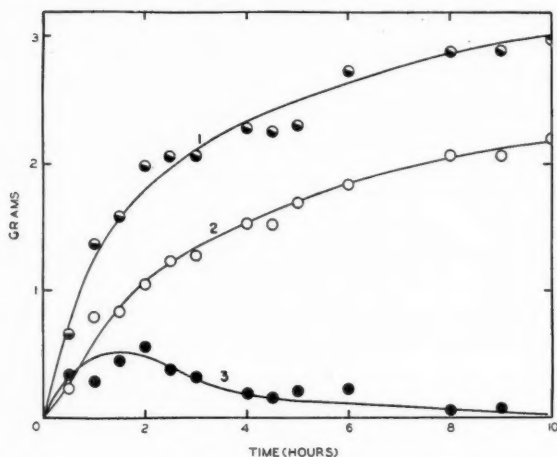
FIG. 7.   *Rate of formation of crude DDT at 0° C.—1;   p,p'-DDT—2, and intermediate alcohol—3.*

Isolation and Characterization of the Intermediate

The previous work of Chattaway and Muir (4) indicated that the probable intermediate in the DDT reaction was 1-(4-chlorophenyl)-2,2,2-trichloro-ethanol (which will be referred to as the alcohol), and therefore this compound was prepared for reference, as previously mentioned.

A sample of the substance indicated by the rate curves to be intermediate in the sulphuric acid condensation was obtained by duplicating on a large scale the procedure used in the rate studies, and distilling the product under reduced pressure.   The yield obtained in this way agreed with that calculated indirectly from the rate studies.   After fractional distillation under reduced pressure, a middle fraction was obtained which crystallized after three months and on recrystallization melted at 44° to 46° C.   A mixture of this material with an authentic sample of the alcohol melted at 45.5° to 46° C.   The material was further characterized by converting it to the acetate, and the product melted at 122.5° to 124° C., the melting point of a mixture of this product with a sample of the acetate being 122° to 124° C.

Thus it appears that the intermediate indicated by the rate data is 1-(4-chlorophenyl)-2,2,2-trichloroethanol, probably contaminated with the ortho-isomer, 1-(2-chlorophenyl)-2,2,2-trichloroethanol.

At 0° C. an increasing degree of purity was observed with acid concentrations of 98.5% or lower, while at 30° C. there was a slight indication of this type of behavior using chloral, chlorobenzene, and sulphuric acid in a molar ratio of 1 : 2 : 3 when the acid concentration was 95.9% or lower.   No trace of intermediate accumulation was apparent at 50° or 70° C. under the conditions investigated.

The Formation of DDT from 1-(4-Chlorophenyl)-2,2,2-trichloroethanol

The reaction between the alcohol intermediate and chlorobenzene in sulphuric acid was studied in a manner similar to that described previously for the chloral–chlorobenzene reaction, by stirring the reactants in 50 ml. flasks placed in a thermostat.   The reaction was quenched and the product was analyzed as usual.

It was found that the yield and rate of DDT production depended on the temperature, sulphuric acid concentration, and amount in much the same way as the chloral–chlorobenzene reaction.   Depending on the reaction temperature used, two types of rate curves have been found; representative ones are plotted in Fig. 8.
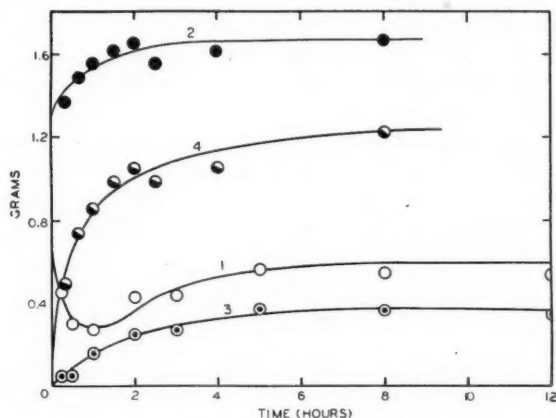

Fig. 8.   *Rate of conversion of intermediate alcohol to crude product at 0° C.—1, at 30° C.—2, and to p,p'-DDT at 0° C.—3, and at 30° C.—4.*

It is apparent that the purity of the crude product increases as the reaction proceeds, but as has been previously pointed out, the p,p'-DDT:total DDT ratio is constant throughout a reaction at a given temperature, so that the observed increase in purity is due to the disappearance of the alcohol concurrently with the formation of DDT.

A closer examination of Fig. 8 shows that at 0° C. the rate of disappearance of the alcohol is greater than the rate of appearance of DDT since the crude weight during the early parts of the reaction is less than the weight of alcohol used initially.   To estimate the extent of loss due to the analytical method, the errors in the various steps have been assessed experimentally.   Washing the chloroform solution of the crude material and distillation of the wet chloroform are sources of considerable error and together may amount to 22%. Hence, 140 mgm. of the 650 mgm. of alcohol put into a normal reaction mixture might be lost.   Since 380 mgm. of crude material has been removed from the reaction mixture in one hour, as shown by the rate curves at 0° C.,

experimental error is not the sole factor responsible for the low crude yields encountered.   It also indicates that, while the crude rate curves are not quantitatively correct, they do indicate the general behavior of the reaction.

A possible explanation of the low yields encountered at 0° C. is the rapid formation of an intermediate compound from the alcohol and conversion of it at a slower rate to DDT.   This material should be water soluble or volatile at 50° C. at 1 mm. of mercury pressure to account for the lower crude yields.

The concentration of this hypothetical intermediate can be calculated as follows: The concentration of the original alcohol in the crude product can be calculated in a manner similar to that used previously in the normal Baeyer condensation; from the constancy of the p,p'-DDT:total DDT ratio and the final purity of 85% achieved in these reactions at 0° C., starting with pure 1-(4-chlorophenyl)-2,2,2-trichloroethanol, the total DDT content of the product can be calculated from the p,p'-DDT yield.   Since the crude product weight represents the alcohol plus DDT, the difference between the weight of crude and the weight of DDT at a given time gives the weight of the alcohol at that time.   The intermediate concentrations can then be derived by adding the percentages of the alcohol present as such and in DDT and subtracting the sum from 100%.   The difference represents the per cent intermediate, and these values, together with the alcohol values, are plotted in Fig. 9.   During
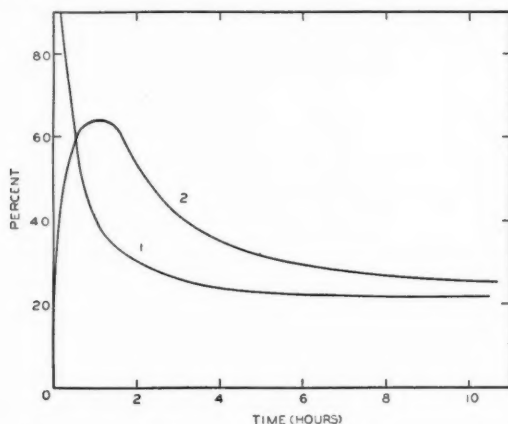
FIG. 9.   *Rate of decrease of the alcohol concentration at 0° C.—1, and intermediate concentration—2.*

the process of calculation from the original data the errors are magnified by multiplication and especially by subtraction of quantities of comparable magnitude.   Consequently, the data used for calculation were taken from the smoothed curves in Fig. 8.

Since the intermediate may be 1-(4-chlorophenyl)-2,2,2-trichloroethyl bisulphate as proposed by Rueggeberg, and since it might be expected to be

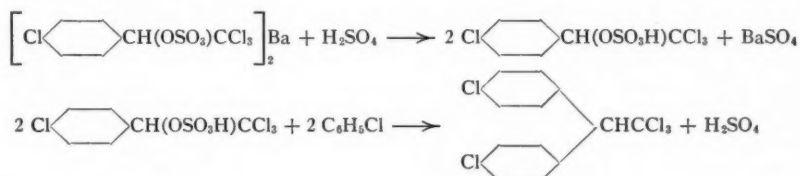water soluble, thus explaining the low crude yields encountered at 0° C., an attempt was made to isolate this material from a normal reaction mixture in the form of its barium salt, but this was not successful.

However, a barium salt has been isolated from the reaction of dioxane sulphotrioxide and the alcohol. Assuming the residue from the ignition of this product to be barium sulphate, the yield of the barium salt of 1-(4-chlorophenyl)-2,2,2-trichloroethyl bisulphate was 43%.

If the free bisulphate ester, 1-(4-chlorophenyl)-2,2,2-trichloroethyl bisulphate, is an intermediate between the alcohol and DDT, its barium salt should form DDT with sulphuric acid and chlorobenzene according to the following series of reactions

$$\left[Cl\!\!-\!\!\bigcirc\!\!-\!\!CH(OSO_3)CCl_3 \right]_2 Ba + H_2SO_4 \longrightarrow 2\ Cl\!\!-\!\!\bigcirc\!\!-\!\!CH(OSO_3H)CCl_3 + BaSO_4$$

$$2\ Cl\!\!-\!\!\bigcirc\!\!-\!\!CH(OSO_3H)CCl_3 + 2\ C_6H_5Cl \longrightarrow \begin{matrix} Cl\!\!-\!\!\bigcirc \\ \qquad\qquad CHCCl_3 \\ Cl\!\!-\!\!\bigcirc \end{matrix} + H_2SO_4$$
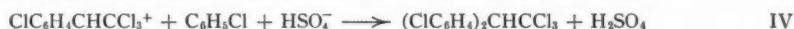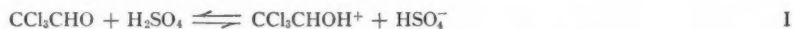
It was found that when 3 gm. of the barium salt was allowed to react with 2 ml. (0.0198 mole) of chlorobenzene and 10 ml. (0.188 mole) of sulphuric acid (101.0% H_2SO_4) a yield of 1.464 gm. of crude DDT was obtained. This represents a 57% yield based on the anhydrous salt of the sulphuric acid ester.

Discussion

Mechanism of the Reaction

The fact that sulphuric acid forms complexes with chloral, and esters with the alcohol, does not necessarily indicate that they are intermediate in a normal Baeyer condensation. There is considerable evidence that aldehydes form oxonium ions in the presence of concentrated sulphuric acid, and also that alcohols form carbonium ions in the same solvent. By analogy it might be expected that similar ions form with chloral and 1-(4-chlorophenyl)-2,2,2-trichloroethanol in the Baeyer condensation so that the reaction mechanism may be presented:

$$CCl_3CHO + H_2SO_4 \rightleftharpoons CCl_3CHOH^+ + HSO_4^- \qquad\qquad\text{I}$$

$$CCl_3CHOH^+ + C_6H_5Cl + HSO_4^- \longrightarrow ClC_6H_4CH(OH)CCl_3 + H_2SO_4 \qquad\text{II}$$

$$ClC_6H_4CH(OH)CCl_3 + 2\ H_2SO_4 \rightleftharpoons ClC_6H_4CHCCl_3^+ + H_3O^+ + 2\ HSO_4^- \qquad\text{III}$$

$$ClC_6H_4CHCCl_3^+ + C_6H_5Cl + HSO_4^- \longrightarrow (ClC_6H_4)_2CHCCl_3 + H_2SO_4 \qquad\text{IV}$$

Since the alcohol accumulates in the crude during the early portions of the reaction at 0° C. with acid concentrations below 98.5% or at 30° C. with low acid amounts and concentrations, the rates of formation of the alcohol and DDT must be about the same; under other conditions the rate of formation of the alcohol must determine the rate of the over-all reaction. Whether

Reaction I or Reaction II involved in the formation of the alcohol is rate determining is not clear, although it may be Reaction I since it involves sulphuric acid which has been shown to have an important influence on the reaction.

This mechanism also explains the low crude yields encountered in the early parts of the reaction of 1-(4-chlorophenyl)-2,2,2-trichloroethanol to form DDT at 0° C. The formation of carbonium ion may proceed to equilibrium at a rate faster than its subsequent reaction to form DDT, so that early in the reaction it is present in the sulphuric acid as carbonium ion. If the sulphuric acid is quenched at this time the carbonium ion will be largely converted to the sulphuric acid ester by the reaction

$$ClC_6H_4CH(OH)CCl_3 + HSO_4^- \longrightarrow ClC_6H_4CH(OSO_3H)CCl_3$$
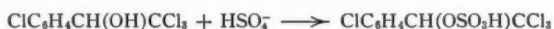
the rate of which is increased by the large concentration of bisulphate ion from dilution of the sulphuric acid. Since the sulphate may be expected to be soluble in this medium it is thus removed from the crude product. This behavior is not encountered at 30° C. because Reaction IV must proceed at a rate sufficient to keep the carbonium ion concentration small.

At acid concentrations near 100% the effect of a still more effective catalyst, sulphur trioxide may be imposed on the sulphuric acid.

Since an increase in the amount or concentration of sulphuric acid or an increase in reaction temperature generally results in lower p,p'-DDT yields, although the time for complete reaction will be shorter, the choice of optimum reaction conditions will depend on the equipment employed. In order to meet purity specifications it may be necessary to recrystallize the crude product, unless the purity is increased sufficiently by using lower temperatures or 4-chlorobenzenesulphonic acid (spent acid containing 4-chlorobenzene-sulphonic acid could be fortified with sulphur trioxide and reused).

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STUDIES ON THE FORMATION OF HEXAMINE FROM FORMALDEHYDE AND AMMONIUM SALTS IN AQUEOUS SOLUTION[1]

By J. R. Polley[2], C. A. Winkler[3], and R. V. V. Nicholls[4]

Abstract

It is shown that the reaction of formaldehyde with an ammonium salt to form hexamine is general. The rate of formation and the final yield of hexamine vary greatly with the different ammonium salts, being greater in the solutions of higher pH. When buffered at given pH, the various ammonium salts give approximately the same rates of formation and final yields of hexamine. Rate curves have been determined for the reaction of formaldehyde with ammonium nitrate in aqueous solutions buffered at pH 8.0, 6.0, and 4.0, at temperatures of 0°, 20°, and 40° C. and over a range of initial mole ratios (formaldehyde: ammonium nitrate) of 0.75 to 3.0. For each set of conditions, three rate curves have been obtained on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride. In excess formaldehyde, it appears that a stable by-product is formed; its formation increases as the temperature is increased. In excess ammonium nitrate, by-product formation is decreased. A mechanism of hexamine formation is suggested in accordance with the data.

Introduction

The kinetics of the reaction between formaldehyde and ammonia in aqueous solution to produce hexamine were first studied by Baur and Rüetschi (1) in 1941 and more recently in greater detail by Boyd and Winkler (2).

Although hexamine has been prepared by the reaction of formaldehyde with certain ammonium salts, in both aqueous and glacial acetic acid solutions (3, 10, 12, 13), there has been no investigation of the kinetics of hexamine formation in such reactions. At least two different reaction sources should be possible. When the formaldehyde functions as a condensing agent, hexamine is formed. Formaldehyde may act, however, as a reducing agent, in which case the salts of methylamines are formed (6, 7).

$$NH_4Cl \xrightarrow{HCHO} CH_3NH_2 . HCl \longrightarrow (CH_3)_2NH . HCl \longrightarrow (CH_3)_3N . HCl + nHCOOH$$
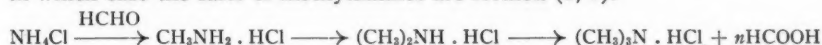
If the reaction of formaldehyde to form hexamine is general with ammonium salts, the equation can be written in the general form:

$$6HCHO + 4NH_3 . HX \longrightarrow (CH_2)_6N_4 + 6H_2O$$

It was proposed in this present work to determine whether the reaction was general for different ammonium salts by investigating the reaction of formaldehyde with numerous ammonium salts in both aqueous and glacial acetic acid media. In particular, it was hoped to isolate and identify hexamine either as such or as one of its salts, but, failing this, to establish its presence in the

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reaction solution by the addition of mercuric chloride to the acidified solution, with a view to precipitating the insoluble hexamine – mercuric chloride complex (8).

Experimental and Results

The isolation of hexamine from various aqueous formaldehyde–ammonium salt solutions was attempted by evaporating them to dryness under reduced pressure at 50° C. The mercuric chloride method indicated the presence of some hexamine in all the reaction solutions, but hexamine was isolated and identified only when ammonium carbonate, acetate, and propionate were used. It was found, however, that hexamine could be isolated in good yield with all the ammonium salts tried, if, before beginning the evaporation under reduced pressure, the reaction solution is made alkaline, for example, by the addition of sodium carbonate, sodium bicarbonate, etc.

Similarly, when the above procedure was used but with a glacial acetic acid solution of paraformaldehyde and the ammonium salt, hexamine was shown to be present in all the reaction solutions but was isolated in good yield only with ammonium acetate, propionate, and carbonate. Hexamine was obtained in good yield with all the ammonium salts tried if the last quarter of the distillation were conducted in the presence of barium carbonate.

Thus, it appears that the reaction of formaldehyde with an ammonium salt to form hexamine is general, the isolation of the hexamine in good yield depending on the neutralization of the acid liberated in the reaction before the reaction solution is evaporated to dryness.

A study was next made of the rate of hexamine formation in aqueous solutions of formaldehyde with different ammonium salts. The reactions were conducted in glass-stoppered Erlenmeyer flasks. The formation of the hexamine – mercuric chloride complex was used for the quantitative estimation of hexamine as it was by Hale (5), Garmaise (4), and Boyd and Winkler (2). The rate of hexamine formation was studied in solutions initially $2.5\ N$ in ammonium salt and $3.75\ N$ in formaldehyde by precipitating the hexamine in 4-ml. samples of the reaction solution after given time intervals by the addition of mercuric chloride solution. The weight of hexamine was determined from a calibration curve between given weights of hexamine and the corresponding weight of the hexamine – mercuric chloride complex.

The rate of hexamine formation from formaldehyde with a series of ammonium salts was investigated by this procedure. The effect of varying the formaldehyde:ammonium salt ratio on the rate of hexamine formation was also investigated. The formaldehyde concentration was doubled in one series of experiments while in another series the ammonium salt concentration was doubled. Fig. 1 shows the rate of hexamine formation with different ammonium salts and Fig. 2 shows the effect of varying the formaldehyde: ammonium salt ratio on the rate of hexamine formation with a given ammonium salt.

It is seen that doubling the formaldehyde concentration beyond that required by the theoretical ratio produces a larger increase in the rate of formation and final yield of hexamine than is observed when the ammonium
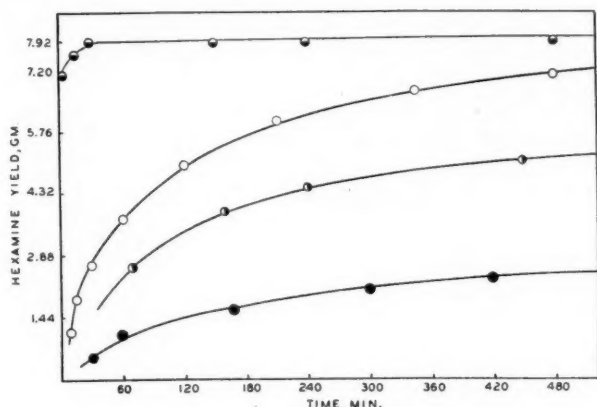

FIG. 1.   *Rate of hexamine formation with different ammonium salts.*
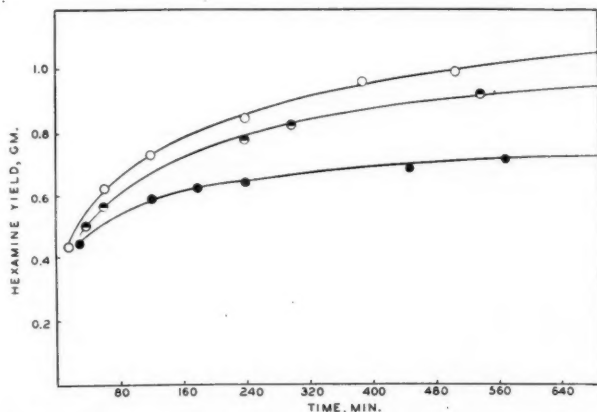●—CH_3COONH_4.   ○—$(COONH_4)_2$.   ◑—$(NH_4)_2SO_4$.   ●—NH_4NO_3.

FIG. 2.   *Rate of hexamine formation at 25° C. in dilute formaldehyde – ammonium sulphate solutions.*
○—*Mole ratio HCHO : NH₃ of 3 : 1.*   ◐—*Mole ratio HCHO : NH₃ of 1.5 : 2.*
●—*Mole ratio HCHO : NH₃ of 1.5 : 1.*

salt concentration is doubled.   It was also noted that the pH of the formalde-hyde – ammonium nitrate solution was lower than that of formaldehyde – ammonium acetate solution, both at the beginning of the reaction and at the end point.   This observation suggested that the pH of the medium might be one of the most important factors governing the rate of formation.

The effect of pH on both the rate of hexamine formation and the final yield was studied in aqueous formaldehyde – ammonium salt solutions by repeating the previous experiments except that this time the solutions were buffered at pH 4.0, 6.0, and 8.0.   Fig. 3 shows the rate of hexamine formation with
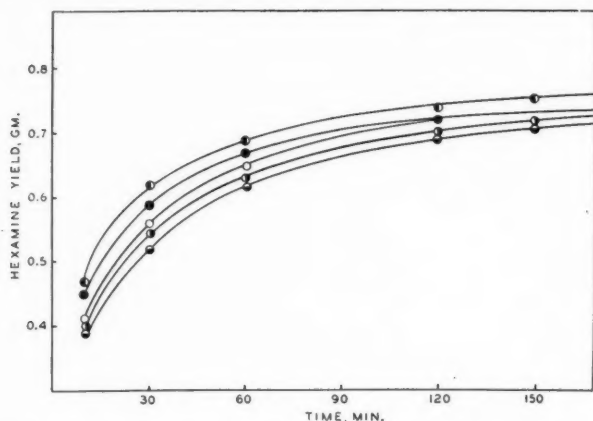
FIG. 3.   *Rate of hexamine formation at 25° C. in various formaldehyde – ammonium salt solutions buffered at pH 4.0.*
     $\mathbb{O}$—$(NH_4)_2HPO_4$.   ●—CH_3COONH_4.   ○—$(COONH_4)_2$. $\mathbb{O}$—$(NH_4)_2SO_4$.
     $\ominus$—NH_4NO_3.
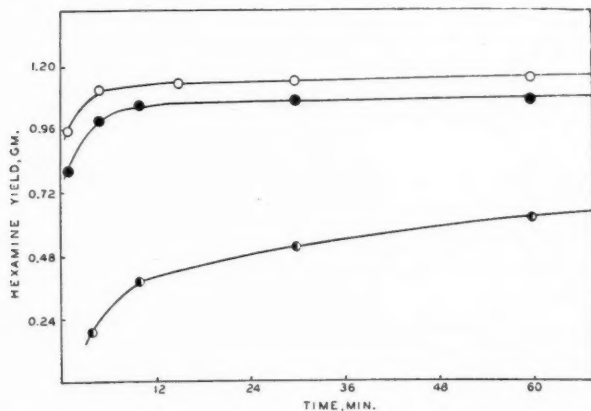

FIG. 4.   *Rate of hexamine formation at 25° C. in buffered formaldehyde – ammonium nitrate solutions.*
     ○—At pH 8.0.   ●—At pH 6.0. $\mathbb{O}$—At pH 4.0.

different ammonium salts when the solutions were buffered at pH 4.0.   Similar results were obtained at pH 6.0 and 8.0.   Fig. 4 shows the effect of pH on the rate of hexamine formation with a given ammonium salt.

These graphs present a striking illustration of the effect of pH on both the rate of hexamine formation and the final yield. In buffered solution, the rates are closely similar for the different ammonium salts used, and the final yields differ by only about 10%, whereas in unbuffered solutions, the yields differ by as much as 60%.

These observations suggest that, at given pH, all the ammonium salts give approximately the same rates of formation and final yields of hexamine, indicating that, at given pH, different ammonium salts lose their individuality and become merely sources of ammonium ions or available ammonia as far as hexamine formation is concerned.

A kinetic study of the formation of hexamine in an aqueous formaldehyde – ammonium salt solution was then made, the rate of disappearance of ammonia and formaldehyde being followed as well as the rate of appearance of hexamine. Since it was shown that at given pH the various ammonium salts show similar rates of hexamine formation, these experiments were made using ammonium nitrate as a representative salt.

Formaldehyde – ammonium nitrate solutions buffered at pH 4.0, 6.0, and 8.0 were used. To facilitate buffering these reactions, the ammonium nitrate concentration was reduced to 0.20 N and the formaldehyde concentration to 0.30 N. The buffer solutions were prepared according to McIlvaine but five times the recommended concentrations were used to ensure an adequate alkali reserve in the buffered solutions. Temperatures of 0°, 20°, and 40° C. were also used. The effect on the rate of formation and the final yield of hexamine of doubling the concentration of the formaldehyde and the ammonium nitrate beyond the theoretical ratio was also studied in the solutions at the pH levels and temperatures indicated above.

The course of hexamine formation in the reaction solutions was followed by removing 4-ml. samples after different times and adding to 20 ml. of acidified saturated mercuric chloride solution. A hexamine – mercuric chloride complex calibration curve was established for each pH of the reaction mixture investigated. This was necessary, since the addition of 4-ml. samples of these different buffered solutions to the mercuric chloride solution resulted in slightly different pH of the medium from which the hexamine was precipitated and this caused a shift in the calibration curve.

The formaldehyde content of the solution was determined by the method of Schulek (11) which is a variant of the well known potassium cyanide method of Romijn (9). The procedure is based on the quantitative formation of cyanohydrin when formaldehyde is treated with a solution containing a known excess of potassium cyanide. The method involves determining the unreacted cyanide by iodimetry.

The residual ammonia, as ammonium nitrate, at any given time in the reaction solution could not be determined directly by the Kjeldahl method since hexamine was also present. Therefore, the method used involved the determination of the ammonia present in the 4-ml. sample for the hexamine

analysis.   After the hexamine – mercuric chloride complex was collected on a tared, sintered-glass crucible, the filtrate was collected for a determination of the residual ammonia.   The excess mercury was precipitated with sodium sulphide solution to prevent the formation of mercury–ammonia complexes. After removing the mercurous sulphide precipitate by filtration, the solution was placed in a 125 ml. Kjeldahl flask and the ammonia determined by the usual Kjeldahl method.

For each set of reaction conditions, three rate curves of hexamine formation were obtained on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride.   In all, this gave rise to 27 graphs but since only three different types of behavior were observed, it is necessary to reproduce only three typical graphs for discussion.
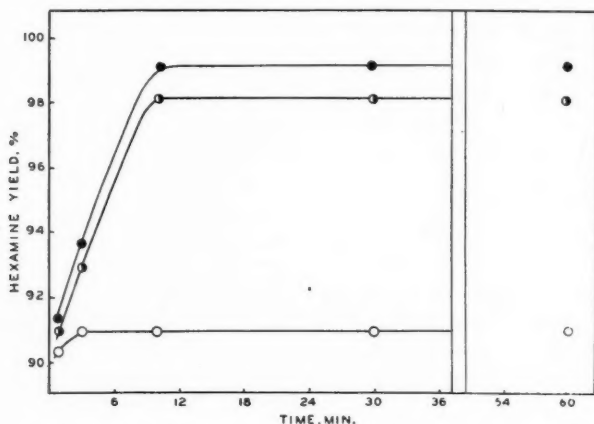

Fig. 5.   Rate curves for reaction at pH 8.0 and 40° C.   Mole ratio formaldehyde : ammonium nitrate of 3 : 1.
●—Yield based on NH₃ consumed.   ◐—Yield based on HCHO consumed.
○—Yield based on precipitate with HgCl₂.

Fig. 5 represents the type of behavior that is observed in excess formaldehyde.   The mercuric chloride curve is about 10% below the formaldehyde curve at the end point, although the curves are in closer agreement initially. The ammonia curve is about 3% above the formaldehyde curve.   The fact that both the formaldehyde and ammonia curves lie above the mercuric chloride curve suggests that more formaldehyde and ammonia are consumed than appear as hexamine.   In view of the manner in which the data are expressed, it would seem necessary to assume the formation of a by-product, the formation of which increases as the temperature is raised but appears to be essentially independent of the pH.   No attempt was made to identify the by-product, the purpose of this study being the conversion of reactants to hexamine.   It would be difficult to isolate and identify a by-product, if

formed, in the presence of formaldehyde, ammonium nitrate, buffering reagents, and hexamine, and at such dilution and in such small amount (the conversion of reactants to hexamine being at least 90%). In excess formaldehyde, the three rate curves differ only slightly at first. With increasing time, however, the mercuric chloride curve indicates that an end point has been reached, while the formaldehyde and ammonia curves continue to rise. This shows that hexamine formation has ceased but formaldehyde and ammonia are still reacting. These observations suggest that, under the reaction conditions investigated, the formation of hexamine is a more rapid reaction than that of by-product formation.
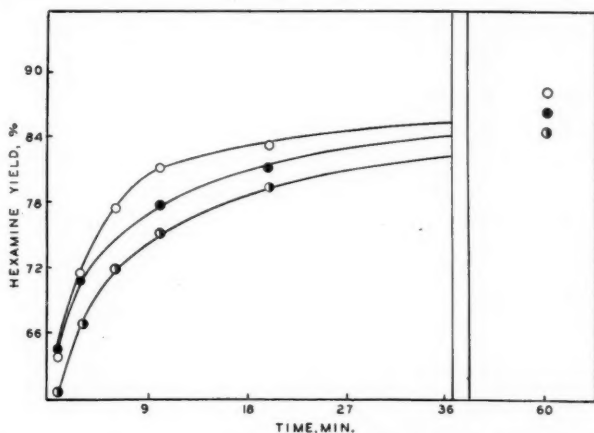

FIG. 6. *Rate curves for reaction at pH 8.0 and 20° C. Mole ratio formaldehyde : ammonium nitrate of 1.5 : 1.*
●—*Yield based on NH₃ consumed.*   ◐—*Yield based on HCHO consumed.*
○—*Yield based on precipitate with HgCl₂.*

Fig. 6 represents the type of behavior frequently observed when the formaldehyde and ammonium nitrate are present in the theoretical ratio and observed in excess ammonium nitrate at pH 8.0. The ammonia curve lies below the mercuric chloride curve but both of these curves lie above the formaldehyde curve. Since it is not possible to have more hexamine formed than can be accounted for on the basis of formaldehyde consumed, it is evident that an explanation must be provided for these analytical results.

One possible explanation is that the hexamine – mercuric chloride complex adsorbs ammonium nitrate or ammonia, thereby adding extra weight to the complex. Actually, however, excess ammonium nitrate does not produce a greater divergence in the curves. An experiment in which hexamine was precipitated in the presence of ammonium nitrate according to the procedure outlined for hexamine analysis showed that there was no co-precipitation or adsorption.

The other possible explanation is that some material other than ammonium nitrate or hexamine is co-precipitated with the hexamine. This would account for the high mercuric chloride curve. The fact that the ammonia curve is also higher than the formaldehyde curve may be explained if the material co-precipitated with the hexamine also contains ammonia, thereby resulting in an abnormally high consumption of ammonia. The observation that the formaldehyde curve lies below the ammonia and mercuric chloride curves may be explained by assuming that, in the analysis of the reaction solution for residual formaldehyde, formaldehyde is analysed out of the material, which may be an intermediate.
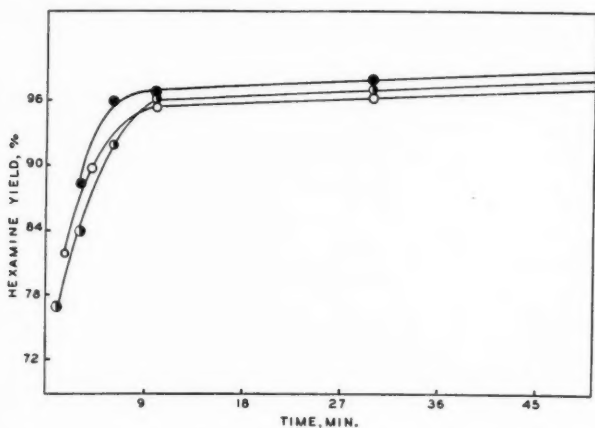

FIG. 7.   Rate curves for reaction at pH 8.0 and 20° C.   Mole ratio formaldehyde : ammonium nitrate of 1.5 : 2.
●—Yield based on NH₃ consumed.   ◑—Yield based on HCHO consumed.
○—Yield based on precipitate with HgCl₂.

Fig. 7 represents the behavior observed in excess ammonium nitrate. The three rate curves are closer together than they are in excess formaldehyde and when the reactants are present in the theoretical proportions for hexamine formation. Thus, whereas excess formaldehyde decreases the conversion of reactants to hexamine, excess ammonium nitrate favors the conversion of reactants to hexamine.

A further important observation disclosed by the data is that doubling the formaldehyde concentration beyond that required by the theoretical proportions for hexamine formation produces a greater increase in the initial rate of hexamine formation than is produced by doubling the ammonium nitrate concentration. Also, the final hexamine yields are usually greater in excess formaldehyde at the lower temperatures. As the temperature is increased, however, the conversion of the reactants to hexamine becomes less complete, so that the yield of hexamine at the end point may be actually decreased.

In their investigation of the aqueous formaldehyde–ammonia system, Baur and Rüetschi (1) followed the course of the reaction only by an acid titration of the ammonia. They favored a mechanism of hexamine formation that involved the formation of methyleneimine and its subsequent trimerization to the postulated intermediate, cyclotrimethylenetriamine. Since they followed only the rate of disappearance of ammonia and did not simultaneously follow the rate of disappearance of ammonia and the rate of appearance of hexamine, it is impossible to compare their results with those obtained in this kinetic study of the aqueous reaction of formaldehyde with ammonium nitrate at various controlled pH.

Boyd and Winkler (2), on the basis of their more detailed kinetic study of the aqueous formaldehyde–ammonia system, proposed a two-path mechanism of hexamine formation, one path being preferred in excess ammonia, the other in excess formaldehyde. Formaldehyde and ammonia are represented as reacting in a series of addition and condensation reactions, excess ammonia leading to the formation of cyclotrimethylenetriamine as intermediate, whereas excess formaldehyde leads to the formation of the methylol form of hemi-hexamine, which on dimerization yields hexamine.
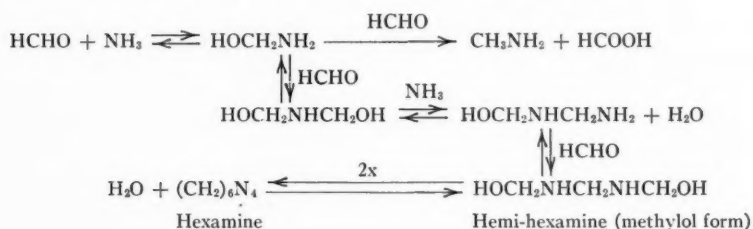
In this present study of the aqueous reaction of formaldehyde with ammonium nitrate at various controlled pH, it has also been found that the three rate curves tend to be in close agreement in excess ammonium nitrate but to diverge in excess formaldehyde. However, whereas Boyd and Winkler found that this effect was reversed at elevated temperature, the data in the present investigation indicate that elevated temperature merely accentuates the tendency for by-product formation, especially in excess formaldehyde. Since, in the work of Boyd and Winkler, the pH of the different reaction solutions was not known nor controlled, it is difficult to say whether the difference between the results is fundamental. In any event, the present study at controlled pH gives no indication of alternative reaction paths leading to hexamine formation.

If it be assumed that the active reagent in the ammonium salt with which the formaldehyde reacts to form hexamine is ammonia, then the equilibrium involving ammonia and hydrogen ion will explain the effect of pH on the rate.

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
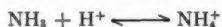
If the active reagent were the ammonium ion, the reaction should proceed readily under conditions favoring the formation of ammonium ions, that is, in acidic solutions. The experimental data, however, show that the reaction is favored in solutions of higher, not lower pH.

On the basis of the data obtained from these experiments, the following mechanism of hexamine formation from the aqueous reaction of formaldehyde with an ammonium salt is suggested.

$$HCHO + NH_3 \rightleftarrows HOCH_2NH_2 \xrightarrow{HCHO} CH_3NH_2 + HCOOH$$

$$\updownarrow HCHO$$

$$HOCH_2NHCH_2OH \xrightarrow{NH_3} \rightleftarrows HOCH_2NHCH_2NH_2 + H_2O$$

$$\updownarrow HCHO$$

$$H_2O + (CH_2)_6N_4 \xleftarrow{2x} HOCH_2NHCH_2NHCH_2OH$$

$$\text{Hexamine} \qquad\qquad \text{Hemi-hexamine (methylol form)}$$

The first intermediate represented is methylolamine, $HOCH_2NH_2$. If formaldehyde reacts with methylolamine in an addition reaction, dimethylolamine, $HOCH_2NHCH_2OH$, is formed. If, however, formaldehyde reacted with it in an oxidation–reduction reaction, methylamine would be formed. The formation of methylamine is represented as an irreversible reaction, since it was shown that hexamine was not formed from it. If it be considered that the methylolamine reacts with ammonia instead of with formaldehyde, methylenediamine, $H_2NCH_2NH_2$, would be formed. This, on reaction with formaldehyde, would also yield the methylol form of hemi-hexamine.

The experimental observation that the rate of hexamine formation is more sensitive to change of formaldehyde concentration than to change of ammonia concentration is then readily explained if it be assumed that the rate of reaction between formaldehyde and amino groups is rate-governing.

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THE ISOLATION OF SASSAFRAS LIGNIN[1]

By W. J. Bond,[2] Irvine G. Goddard,[3] and George F Wright[4]

Abstract

Since the sassafras tree yields oils which are rich in safrole, it might be expected that the lignin from the wood would contain the piperonyl nucleus. This lignin was extracted from the wood with hot acetic acid and was found to resemble lignins from other deciduous woods in methoxyl content and solubility. It did contain much combined carbohydrate which seemed to be pectic in nature, since it was removed by boiling formic acid with evolution of carbon dioxide and formation of furfural. No piperonylic acid could be isolated from these lignin fractions by alkaline permanganate or hydrogen peroxide oxidations. Sassafras ligninsulphonic acid was prepared and then distilled with alkali but no piperonal was found in the distillate. According to these criteria, sassafras lignin contains none of the methylenedioxy linkage characteristic of the piperonyl nucleus.

In 1927 Freudenberg (4) suggested that lignin contained a methylenedioxy linkage, since he obtained 0.2 to 1.2% yields of formaldehyde by distilling suspensions of beech or spruce lignins with 12% hydrochloric acid. He considered that this methylenedioxy group was linked as in piperonal, I, an analogue of the vanillin and syringaldehyde which have been isolated from spruce and birch lignins (5).

I
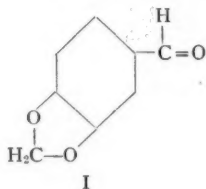
Sarkar (8) also concluded that this linkage was present in the lignin molecule. By distillation of jute lignin with 28% sulphuric acid he was able to obtain formaldehyde yields as high as 2.6%.

Phillips and Goss (7), on the other hand, found that, while Freudenberg's results could be checked in the case of spruce lignin, other lignins, prepared in different ways, gave varying amounts of formaldehyde, and some lignins gave no formaldehyde. It appeared to them that both the source of the lignin and its method of isolation were factors governing the formaldehyde yield.

When Hunter, Wright, and Hibbert (6) subjected substances like piperonal, dihydrosafrole, and piperonylic acid to some of the extraction conditions used for isolation of lignin, they found that 75 to 88% of the aromatic compounds could be recovered unchanged. This indicated that unaltered methylenedioxy

linkages might be expected in lignins. They found, however, that the 12% hydrochloric acid used by Freudenberg was not very effective toward splitting of formaldehyde from piperonylic acid although 28% sulphuric acid effected a scission which was almost quantitative.

They ascertained further that many carbohydrates yielded formaldehyde, as well as furfural, when boiled with acid. Since these two aldehydes were also isolated concomitantly from a number of lignins, they concluded that they were formed from carbohydrate incompletely removed from (or intrinsic with) the lignins. Freudenberg (3) questioned this conclusion, although he points out that cinnamyl alcohol types rather than methylenedioxy types may be the source of his formaldehyde.

It occurred to the present authors that, of all lignins which might be expected to contain the methylenedioxy linkage, that isolated from sassafras wood ought to be the richest in this characteristic, since the oils from this wood are rich in safrole (10). The methods which yield vanillin and vanillic acid from woods like spruce, birch, and oak (whose oils are rich in guaiacyl compounds) ought then yield piperonal and piperonylic acid from sassafras lignin.

Sassafras xylem reduced to 25 mesh was extracted exhaustively with benzene–ethanol and from separate portions were then extracted acetic acid lignins (1), and ligninsulphonic acid.

These extractions were normal in every respect except that more trouble was encountered in freeing the isolated lignin from carbohydrate than was experienced with spruce or birch wood. Acetic acid extracted 24% of the weight of the wood as lignin, but this lignin contained combined carbohydrate. Much of this carbohydrate, which seemed to be of a pectic acid nature, could be liberated by further digestion with 95% formic acid.

The acetic acid lignin was fractionated. Successive Soxhlet extractions of this acetic acid lignin with ether, benzene, and chloroform removed 14, 16, and 70%, respectively, of the total lignin, the corresponding methoxy contents being 21.9, 20.8, and 19.5%. These values resemble those obtained for comparable values of birch lignin. Since a cyclic acetal such as is found in piperonal gives no methyl iodide in the Zeisel determination it is evident from these methoxyl values that the methylenedioxy linkage is not present instead of methyl ether linkages to any appreciable extent.

The lignin sulphonic acid was prepared from the sassafras xylem by a standard cooking procedure. The liquor was then boiled with alkali and the aqueous distillate continuously extracted with benzene and then returned to the boiling alkaline solution. This variation from the prescribed procedure (9) would be expected to separate piperonal, which is volatile in boiling aqueous alkalis, from vanillin and syringaldehyde which are not volatile. However, no residue remained after evaporation of the benzene. Since piperonal was shown to be stable to alkaline heating and to respond to the extraction procedure, it is probable that no piperonyl linkage is present in sassafras ligninsulphonic acid.

A further attempt to discover the presence of the piperonyl nucleus was made by oxidation of the sassafras lignin. Although alkaline potassium permanganate would convert piperic acid (2) to piperonylic acid in 66% yield, a comparable oxidation of the ether-soluble fraction of the lignin yielded none of this easily sublimed acid.

In connection with these oxidation studies, it was found that alkaline hydrogen peroxide would oxidize piperonal in 88% yield to piperonylic acid, although it would not attack piperic acid. The strong hydrogen peroxide (15%) did, however, attack the lignin smoothly and efficiently in alkaline solution. When piperonal to the extent of 1.2% was added to the lignin, it was recovered from the oxidizing medium as a 48% yield of piperonylic acid. On the other hand no trace of this acid was obtained from the lignin alone.

In view of these results it would seem doubtful that sassafras lignin contains a measurable amount of the piperonyl nucleus.

Experimental

Preparation and Purification of the Woodmeal

A sassafras tree, approximately 15 years old (27 rings) growing at Simcoe, Ontario, was found in a clearing on sandy loam soil. A 28 in. section of the tree trunk, 5 to $5\frac{1}{2}$ in. in diameter, about 40 in. from the soil surface, was taken.

The bark and cambium were carefully removed and the xylem, first made into shavings by means of a lathe and chisel, was put through a Wiley mill to prepare the woodmeal (25 mesh). The woodmeal was air-dried; it contained about 9.4% moisture.

Extraction of Sassafras Woodmeal with Acetic Acid

A suspension of 400 gm. of this purified sassafras woodmeal in 2.5 litres of glacial acetic acid was stirred under reflux for 100 hr. During this period, 4.2 cc. (N.T.P.) of carbon dioxide was evolved per gram of woodmeal. Finally 233 gm. of residual woodmeal was filtered off through linen cloth and washed with acetic acid. The filtrate and washings were concentrated to a volume of about 350 cc. (10 to 15 mm.) and then poured into 2 litres of water. The lignin precipitated in this manner was filtered off by gravity and washed with 35 litres of water until free from carbohydrate by Molisch test. There was some tendency toward peptization; the colloidal lignin in the first 5 litres of filtrate was precipitated by boiling, after addition of sodium sulphate, until the volume was 200 cc. The distillate gave a strong furfural test. The aqueous residue, from which the coagulated lignin was filtered, was extracted with 150 cc. of ether. The extract was distilled to yield 0.83 gm., b.p. 120° to 180° C. (0.001 mm.), which did not crystallize after six months. No piperonylic acid could be isolated after the oxidation of this distillate (in alkaline solution) with 200 ml. of 2% potassium permanganate solution. Oxidation of piperic acid under the same conditions, gave a 66% yield of piperonylic acid, m.p. 226° C.

The total of the precipitated lignin was dried at 50° to 60° C. (10 mm.) to weigh 81 to 84 gm. or 23 to 24% by weight of the oven-dry woodmeal. Although this material had been washed free from water-soluble carbohydrate, it undoubtedly contained combined carbohydrate, since a suspension in water gave a positive Molisch test. It was soluble in acetic and formic acids, ethyl acetate, acetone, dioxane, chloroform, pyridine, and dilute alkali. It was partly soluble in ether, benzene, methanol, and ethanol.

Fractionation of Acetic Acid Sassafras Lignin

Fractionation was carried out in a Soxhlet extractor, using ether at 760 mm., benzene at 200 mm., and chloroform at 250 mm. in this succession. The three solvent fractions, which comprised almost all the lignin, were evaporated, finally in a dry air stream, except for aliquot portions which were precipitated into petroleum ether (b.p. 28° to 38° C.) for methoxyl determination.

Removal of Combined Carbohydrate from the Chloroform Fraction

In order to remove the combined carbohydrate from the least soluble, chloroform fraction, 67 gm. of this lignin was boiled under reflux in 350 cc. of 95% formic acid for 18 hr. This treatment liberated 6.2 cc. of carbon dioxide per gram of lignin used. The solvent was distilled off completely under 15 mm. pressure. The residue was washed with two litres of water to remove soluble carbohydrate (positive Molisch test and two osazones, m.p. 172° to 174° C. and 155° to 156° C.) and then with ether to remove furfural and other ether-soluble material. The residual lignin weighed 38.5 gm. after drying at 50° to 60° C. (10 mm.). A solution of 1 gm. of this lignin in 9 : 1 acetone–water (15 cc.) was precipitated in a fine stream into 200 cc. of stirred anhydrous ether. Its methoxyl content was 17.4%.

Absence of Piperonal in Sassafras Ligninsulphonic Acid

A suspension of 5.0 gm. of solvent-extracted dry sassafras woodmeal was cooked in a glass bomb tube with 70 cc. of sodium bisulphite cooking liquor containing 6% total and 1.2% combined sulphur dioxide. The temperature was raised to 125° C. over a three hour period and maintained at 120° to 135° C. for 12 hr.

The cooled suspension was filtered to remove 2.8 gm. of extracted meal (56% of total). The filtrate was boiled for 12 hr. with 6% aqueous sodium hydroxide solution in a flask which was equipped with a modified Soxhlet extractor surmounted by a reflux condenser. The modification of the Soxhlet extractor involved an air-vented vertical outlet sealed to the top of the tube which normally would return solvent. Since this dispensed with the siphoning action, a layer of benzene could be maintained over a water seal in the body of the extractor. This benzene thus continuously extracted the aqueous distillate, which then returned to the boiling flask.

Treatment of the ligninsulphonic acid in this way yielded no trace of piperonal in the benzene layer, but when 0.5 gm. of piperonal was cooked with 250 cc. of 6% aqueous sodium hydroxide for 12 hr. in this extractor, the

recovery was 0.24 gm. (48%) of material, m.p. 34° to 35° C. The identity of this recovered piperonal was authenticated by preparation of the 2,4-dinitrophenylhydrazone, m.p. 260° C.

Oxidation with Potassium Permanganate

A total of 27.9 gm. of potassium permanganate was required at the rate of 6 gm. per hour to oxidize a 2.5% alkaline solution of 20 gm. of chloroform-soluble formic acid lignin at 5° C. Although subsequent acidification of the filtrate showed that 95% of the lignin had been oxidized, no piperonylic acid could be isolated by sublimation of the continuous ether extract. Under identical conditions, piperonal was oxidized to piperonylic acid in 66% yield.

Oxidation with Alkaline Hydrogen Peroxide

A solution of 10 gm. of ether-soluble sassafras lignin in 750 cc. of 10% aqueous sodium hydroxide solution was added proportionately over four hours with 670 ml. of 26% hydrogen peroxide to a flask equipped for rapid stirring. The temperature was maintained at 30° to 40° C. and a trace of petroleum ether (b.p. 60° to 70° C.) was added to reduce foaming. After 12 hr. the temperature was increased to 78° C. until foaming (destruction of hydrogen peroxide) had ceased and a negative peroxide test was obtained. The slightly turbid solution which resulted after acidification was continuously extracted with ether. This ether extract, dried with anhydrous sodium sulphate, was subsequently sublimed at 100° to 240° C. (10 mm.). Although oxalic acid, succinic acid, and a low melting solid (m.p. 30° to 50° C.) could be isolated from the sublimate, no piperonylic acid was found. Under otherwise comparable conditions 10 gm. of ether-soluble lignin plus 0.12 gm. of piperonal yielded 0.061 gm. of piperonylic acid, m.p. 210° to 215° C. This 48% crude yield was washed with a little ether to free it from oily impurity, after which it melted at 228° to 229° C. A mixed melting point with authentic material was not lowered.

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A RAPID COLORIMETRIC METHOD FOR THE DETERMINATION OF LYSINE IN PROTEIN HYDROLYSATES[1]

By M. Boulet,[2] J. A. Nelson,[3] and W. D. McFarlane[4]

Abstract

A solution of chlorinated lysine develops a blue color when heated with phosphomolybdic–phosphotungstic acid. This color reaction, which will detect lysine at a concentration of 1 p.p.m., has been made the basis of a sensitive and rapid colorimetric method for the determination of lysine. Lysine and arginine are quantitatively separated from the other amino acids in a protein hydrolysate by adsorption on Decalso and the lysine content of the eluate is determined in the presence of arginine (which does not give the color reaction) by applying the color reaction after chlorination. Satisfactory recoveries of added lysine have been obtained from mixtures of amino acids and from a gelatin hydrolysate. The lysine content of several proteins has been determined and the results compared with those in the literature. In general the values obtained by the colorimetric method are intermediate between those obtained by isolation procedures and those by microbiological methods. The result of a determination on crystalline bovine serum albumin checked closely with the value obtained by the isotope dilution method.

Introduction

It was observed in this laboratory that if an aqueous solution of lysine is treated with a solution of sodium bromate–bromide in hydrochloric acid and the excess bromine removed with sodium arsenite, the resulting product gives an intense blue color when heated with Folins uric acid reagent (phospho-18-tungstic acid). This color reaction will detect lysine in a concentration of 1 p.p.m. Colors of varying intensity are also given by serine, threonine, phenylalanine, tyrosine, tryptophane, cystine, methionine, proline, hydroxy-proline, leucine, histidine, and ornithine. No color is given by glycine, alanine, aspartic and glutamic acids, norleucine, valine, and arginine.

We also found that lysine and arginine are quantitatively separated from the other amino acids in a hydrochloric acid hydrolysate of proteins when, after the hydrolysate has been freed from excess hydrochloric acid by vacuum distillation, the residue is dissolved in 10% aqueous pyridine and the solution passed through a column of Decalso. Arginine and lysine are strongly adsorbed, histidine and ammonia are weakly adsorbed, and the other amino acids are not adsorbed. The traces of histidine and ammonia are washed out of the column with 10% aqueous pyridine and the arginine and lysine are then recovered by elution with dilute hydrochloric acid or $0.2\ M$ sodium carbonate solution.

After treating the hydrochloric acid eluate with a solution of sodium bromate–bromide in dilute hydrochloric acid and removing the excess bromine with sodium arsenite, the color reaction can be applied to determine lysine in the presence of arginine. Ornithine interferes but it is not present in acid hydrolysates of proteins, with the unique exception of tyrocidine (7). Hydroxylysine probably gives the reaction but it is rarely present in significant amounts.

A sensitive and rapid colorimetric method was developed (10) and satisfactory recoveries of added lysine were obtained from mixtures of amino acids and from a gelatin hydrolysate. The lysine content of several purified proteins was determined, and the values obtained were generally intermediate between those obtained by isolation procedures and those by microbiological methods. The result of an analysis of crystalline bovine serum albumin checked closely with the value obtained by the isotope dilution method.

The method was submitted to workers in other laboratories and to other workers in this laboratory. Several reports mentioned encountering difficulties due to the uncertainty of the bromination reaction. In repeated tests with the same solution of lysine, bromination for varying periods of time did not always give maximum reaction in the same reaction time, so that an error of 10% could easily occur unless several determinations were made on the same sample. It was, therefore, decided to investigate the method further with a view to stabilizing the bromination reaction.

The Reaction of Bromine with Lysine

The details of the procedure (10) were based on the knowledge that the bromination reaction was influenced by time, concentration of bromine, and the amount of lysine present. The reaction time for optimal color development was inversely proportional to the concentration of bromine. These facts suggested that an unstable intermediate product was formed in the reaction between bromine and lysine, and this intermediate combined with the phenol reagent to produce the blue compound, whereas its decomposition product did not give the color reaction. Because of this secondary reaction the time of bromination had to be closely controlled.

In an attempt to stabilize the reaction, the hydrogen ion concentration was varied by adding acid or alkali to the lysine solution. When 1 ml. N hydrochloric acid was added before bromination, the reaction was slowed down and the maximum, as measured colorimetrically with the phenol reagent, was only 60% of the value obtained under the standard conditions of bromination. The addition of alkali accelerated the reaction but the yield decreased rapidly with time. With increasing time of bromination the amount of reducing substance, as measured colorimetrically with the phenol reagent, reached a maximum and then decreased. This indicated that the substance that reduced the phenol reagent was formed as an intermediate and that at least two steps were involved in the complete reaction.

When the hydrochloric acid in the brominating reagent was replaced with sulphuric, phosphoric, or hydrobromic acid the reaction rate was markedly decreased, and the maximum reaction was obtained in two to three hours instead of two to three minutes. Furthermore, the maximum color intensity was much less when these acids replaced hydrochloric acid.

Evidently hydrochloric acid plays an important role in the bromination reaction and cannot even be replaced by hydrobromic acid. It may act as a catalyst or as a source of free chlorine, since it is known that free chlorine and free bromine are produced when bromic acid ($HBrO_3$) reacts with hydrochloric acid. Solutions of lysine treated with a solution of pure bromine in $0.2\ N$ hydrochloric acid for periods up to 20 min. at room temperatures gave practically no color with the phenol reagent. The reaction with lysine may, therefore, be due to chlorine rather than bromine.

Chlorination of Lysine

The reagent was prepared by bubbling electrolytic chlorine gas from a cylinder through $0.2\ N$ hydrochloric acid. Standard solutions of lysine were chlorinated for varying periods of time, the excess chlorine removed with sodium arsenite solution, and the color developed with the phenol reagent. The results are given in Fig. 1, in which the colorimeter readings are plotted against reaction time. It will be seen that the reaction reached completion
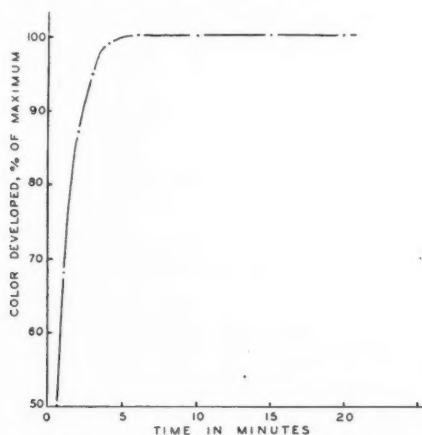
FIG. 1.   *Chlorination of lysine for varying periods of time (lysine concentration = 2.88 μgm. per ml.).*

in four minutes and apparently the chlorination product is stable for at least 20 min. The yield, and hence the sensitivity of the reaction, is comparable to that obtained with the original bromine reagent.

Variable results were obtained with chlorine prepared by oxidizing concentrated hydrochloric acid with manganese dioxide and purified by washing with a 5% solution of potassium permanganate. This was found to be due to

the presence of chlorine dioxide, and the difficulty was eliminated by bubbling the chlorine through a 20% solution of barium chloride instead of the permanganate solution.

When chlorine was substituted for the bromine reagent in the determination of the lysine content of various proteins, the results obtained were substantially the same. However, the chlorination procedure is much simpler and more dependable.

Description of the Method

Reagents

(1). Decalso:— Sodium form of Decalso +40 to 60 mesh (Permutit Co. N.Y., water softener).

(2). Sodium chloride solution:—3 gm. sodium chloride (reagent grade) per 100 ml.

(3). Pyridine solution:—100 ml. of redistilled pyridine (b.p. 114° to 115° C.) diluted to 1 litre with distilled water. The solution is allowed to stand for a few hours before use, to permit the escape of air bubbles.

(4). Sodium carbonate solution (0.2 *M*):—2.12 gm. sodium carbonate (reagent grade) per 100 ml.

(5). Hydrochloric acid (2.0 *N*):—prepared by diluting constant boiling hydrochloric acid.

(6). Chlorine solution:—electrolytic chlorine gas from a cylinder, or chlorine gas generated by adding 3 gm. manganese dioxide to 12 ml. concentrated hydrochloric acid at a temperature not above 20° C., is bubbled through a 20% solution of barium chloride into 50 ml. 0.2 *N* hydrochloric acid for about 20 min. The chlorine solution should be used within one hour of its preparation.

(7). Sodium arsenite:—5 gm. sodium arsenite dissolved in 100 ml. water. The solution is freshly prepared each week.

(8). Mixed alkali:—A solution containing 2 gm. sodium citrate (reagent grade) and 4 gm. sodium phosphate dodecahydrate (reagent grade) per 100 ml.

(9). Phenol reagent:—prepared according to Folin and Ciocalteu (6) but with 100 gm. lithium sulphate monohydrate instead of 150 gm. per litre.

Preparation of the Adsorption Column

A weighed amount of Decalso (700 mgm.) is transferred to a beaker and washed by decantation three times with 3% sodium chloride, and then with distilled water until free from chloride. The adsorption apparatus consists of a 3 in., long stem Pyrex glass funnel, which has been constricted at the outlet. A small pad of cotton is inserted in the stem at the bottom, 25 ml. of water is poured into the funnel, and the adsorbent, suspended in water, is immediately added. By tapping the funnel gently an air-free column about 10 cm. long is obtained. A thin pad of cotton is placed on top of the column

and the excess water is poured out of the funnel by tilting.   The column is washed with 5 ml. of 10% pyridine and is ready for use.   If the amino acid solution is not added without delay the column must be kept under liquid.

Hydrolysis

A sample of protein, containing 2 to 15 mgm. of lysine, is refluxed with 10 ml. of 6 N hydrochloric acid for 24 hr.   The hydrolysate is evaporated *in vacuo* to dryness.   The residue is taken up in exactly 10 ml. of 10% pyridine and the suspension filtered.

Adsorption

One millilitre of the amino acid solution containing 0.3 to 1.5 mgm. of lysine is passed through the column until a depth of about 1 mm. of solution remains above the surface of the adsorbent and three 1 ml. aliquots of 10% pyridine are added successively to wash all the lysine into the Decalso.   The column is then washed with an additional 100 ml. of 10% pyridine and the pyridine washed out of the column with 4 ml. distilled water.   The filtrates are discarded and the lysine and arginine eluted with 20 ml. 0.2 M sodium carbonate solution, the eluate being collected in a 50 ml. volumetric flask.   A small piece of indicator paper is added to the contents of the flask, the hydrogen ion concentration adjusted to pH 3 to 4 with 2 N hydrochloric acid, and the solution finally diluted to volume with distilled water.

Chlorination and Colorimetry

A 1 ml. aliquot of the lysine solution containing 5 to 30 μgm. of lysine is carefully measured into a 10 ml. graduated glass-stoppered Pyrex cylinder and 1 ml. of the chlorine solution is added.   After allowing to stand for five minutes, 1 ml. of the sodium arsenite solution is added.   The mixed alkali solution is then added from a microburette in amount sufficient to adjust the solution to pH 6.2 to 6.5; usually 1.5 ml. is required.   The solution is diluted to 9 ml. with distilled water, mixed, and the cylinder placed in a water bath at a temperature of at least 90° C. but not boiling.   After a few minutes, 1 ml. of the phenol reagent is added from a slow delivery pipette (about 1 ml. in 15 sec.), the liquid being allowed to flow down the wall of the cylinder. The heating is continued for 40 min. and the solution cooled to room temperature.   It is important that the phenol reagent be added in the manner indicated, without removing the cylinder from the bath and without mechanical mixing.

The color intensity is measured with an Evelyn photoelectric colorimeter using a 660 mμ filter.   A reagent blank, prepared by carrying out the chlorination and colorimetry with the reagents alone, is used to obtain the 'centre setting' of the colorimeter prior to reading the test solution.   The lysine content of the solution may be obtained by reference to a calibration curve (Fig. 2) prepared from readings obtained with standard solutions of $l(+)$-lysine monohydrochloride, A.P. grade (Amino Acid Manufacturers, University of California at Los Angeles), containing 0.5 to 3 mgm. lysine per 100 ml., which had been carried through the procedure, including adsorption

on Decalso. The most reliable procedure is to carry out simultaneously a control determination with a standard solution containing approximately the same amount of lysine as that contained in the protein hydrolysate. From
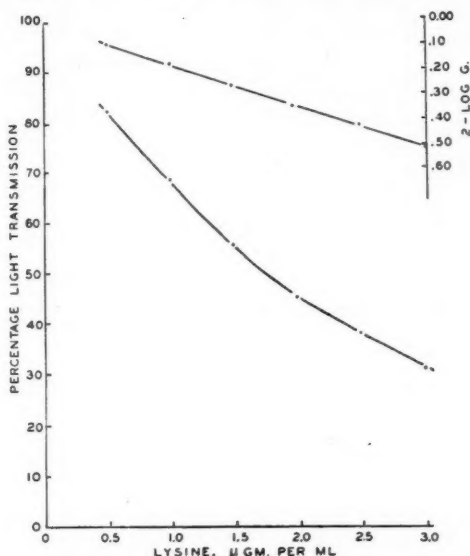

FIG. 2. *Calibration curve and application of Beer's law, K. = 0.167 ±0.003.*

the reading with the standard solution, Beer's law constant, K, is calculated from the relation $K = \dfrac{2 - \log G}{C}$, where C is the concentration of lysine in micrograms per millilitre of standard solution and G is the galvanometer reading. The intensity of the blue color obeys Beer's law over a range of concentrations of 1 to 3 μgm. of lysine per ml. but deviates slightly at lower concentrations.

Application of the Method

Satisfactory recoveries of added lysine from a mixture of pure amino acids and from a gelatin hydrolysate have been obtained; the results are presented in Table I. The lysine content of a number of isolated proteins, as determined by the colorimetric method, is given in Table II.

The sample of casein was prepared according to Cohn and Hendry (4). The lysine content, as determined by the colorimetric method, is slightly higher than the values recorded in the literature for the lysine content of casein as determined by isolation procedures. Vickery and White (18) isolated 6.25% lysine from casein; Plimmer and Lowndes (13), 6.13%; Block, Jones, and Gersdorff (3), 6.50%; Ayre (1), 6.09%; Beach *et al.* (2), 6.20%; and Tristram (16), 6.44%. These workers had at their disposal all

TABLE I

RECOVERIES OF ADDED LYSINE FROM A SOLUTION OF PURE AMINO
ACIDS AND FROM A GELATIN HYDROLYSATE

Sample analyzed	Total lysine, mgm.		% Recovery of added lysine
	Added	Determined	
Amino acid mixture[1]	4.00	4.05	101.2
" " "	4.00	4.10	102.5
0.1754 gm. gelatin	—	8.47	—
0.3847 gm. "	—	18.25	—
0.3680 gm. "	8.00	25.50	99.1
0.1324 gm. "	12.58	18.64	98.2

[1] *The mixture was composed of 10 mgm. histidine monohydrochloride and 5 mgm. each of glycine, hydroxyproline, leucine, serine, aspartic acid, glutamic acid, proline, alanine, phenyl-alanine, valine, tyrosine, norleucine, arginine, methionine, cystine, and threonine.*

TABLE II

LYSINE CONTENT OF PROTEINS AS DETERMINED BY THE COLORIMETRIC METHOD

Material	Sample weight for lysine determination, gm.	Ash[1]	Nitrogen[2]	Lysine[2]
Casein	0.0730	1.50	15.36	7.16
	0.0716			7.14
Lactalbumin	0.0726	0.65	15.02	9.12
	0.0581			9.16
Edestin	0.4120	1.32	18.45	2.71
	0.2779			2.78
Gelatin I	0.1754	1.44	17.76	5.41
	0.3843			5.33
Gelatin II	0.5969	Nil	17.52	5.30
Crystalline serum albumin (bovine)	0.0708	—	16.10	12.43
	0.0609	—	—	12.45
	0.0889	—	—	12.46

[1] *Percentage of moisture-free sample.*

[2] *Percentage of moisture and ash-free sample.*

the advantages of improved procedures and data regarding the numerous losses due to the slight solubility of the various compounds.

However, our value is lower than that obtained by Dunn *et al.* (5), employing their microbiological method, and by Zittle and Eldred (19) and Neuberger (11) employing the decarboxylase method. On a comparable basis (corrected for ash and volatile matter) their values are 8.30, 7.8, and 7.5%, respectively, whereas our average value is 7.15% lysine. Collaborative studies on the

determination of lysine by the microbiological, enzymic, colorimetric, and classical methods should be conducted on the same sample of the highest obtainable degree of purity, to arrive at a generally acceptable value for the lysine content of casein. The possibility that the lysine content of casein preparations is variable, as has been suggested in the case of tryptophane (14), should also be investigated.

The lactalbumin was prepared by the method outlined by Plimmer and Lowndes (13). The other proteins were commercial preparations, i.e., edestin (Eimer and Amend) and gelatin (Baker and Adamson). The second sample of gelatin was purified according to the procedure of Loeb (8, pp. 34-36) for ash-free gelatin. The values for the lysine content of these proteins, as determined by the colorimetric method (Table II) are in good agreement with the values reported in the literature and obtained by isolation procedures (12, 13, 15, 17). The crystalline bovine serum albumin was from the same sample analyzed by Shemin (15) by the isotope dilution method, and it was found to contain 12.42% lysine.

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THE THERMAL EXPLOSION OF LEAD AZIDE[1]

By A. S. Hawkes[2] and C. A. Winkler[3]

Abstract

The minimum explosion temperatures for service and dextrin azides (about 315° C. and 275° C., respectively) are increased considerably by increase of surface: volume ratio of the container and by compressing or wetting the charge with dibutyl phthalate before explosion. When wetted, the two azides were found to be similar in respect of minimum explosion temperatures and induction periods prior to explosion. Sensitization of service azide by preheating was found to be permanent. A limit to sensitization below the minimum explosion temperature was observed, and probably exists also for sensitization above this temperature. Wetting the charge with phthalate nullifies the sensitization. Although dextrin azide alone is more thermally sensitive than service azide, mixtures of the two containing 70% or more service azide show a sharp change to service azide properties; the mixtures apparently are not exploded by the dextrin azide they contain. The value of E in the expression $\ln t = \dfrac{E}{RT} + $ constant, where t is the induction period, has been determined for both the initial and final stages of reaction preceding explosion and found to be essentially unaltered. Minimum explosion temperature of single large crystals was shown to increase with crystal size. The data are interpreted as showing that the thermal explosion of lead azide may result from self-heating, the heat of the pre-explosion reaction not being sufficiently dissipated from the material.

Introduction

The thermal explosion of pure lead azide has been found (1, 8, 19) to have three characteristics of particular interest. (i) There is an induction period, followed by rapid reaction which may or may not lead to explosion, depending on the temperature. (ii) Spontaneous or self-heating of the solid occurs during the decomposition (1, 19). (iii) Samples of pure azide that have been heated and quenched by chilling before explosion occurs require a shorter period of heating a second time to produce explosion (19). Such samples have been termed 'sensitized'.

In addition to pure ('service') azide there is a material also prepared that is precipitated in the presence of dextrin ('dextrin azide'). Service and dextrin azide are crystallographically identical by X-ray examination, but, whereas service azide crystals are generally whole or twinned, the dextrin grains consist of agglomerates of minute crystallites. The two types have been found (19) to differ considerably in their behavior to thermal decomposition. Dextrin azide is capable of explosion at about 275° C., some 40° C. lower than service azide, and, while service azide at suitably chosen temperatures may exhibit induction periods of over a minute, the dextrin material generally shows

induction periods of not more than 12 to 14 sec. From the effect of temperature on the induction period and application of the relation $\ln t = \dfrac{E}{RT} + \text{constant}$, where t is the induction period, and E is the activation energy, values of E of 41.3 and 23.4 kcal. for service and dextrin azides respectively were obtained (19). The difference was accounted for on the basis of a greater number of active centres on the larger available surface of the dextrin azide. Data to be presented later indicate that values of E so obtained should not be interpreted in the sense of a true activation energy for the reaction leading to explosion of lead azides.

Studies on explosions in solids such as the azides of the alkali and alkaline earth metals, as well as lead azide, mercury fulminate, and others, have resulted in dissimilar views about the mechanism whereby explosion is initiated and propagated in such systems (2-12, 14-18). Probably the diversity of opinions merely reflects an inadequate and too flexible experimental background. It was mainly with a view to supplementing the comparatively meagre experimental data that the present study was made.

Experimental and Results

Apparatus

A. *Bulk Detonation*

For experiments with bulk material, the apparatus was similar to that used by Ubbelohde (19). The heating bath consisted of an electrically heated block into which was drilled a hole to contain melted tin as the thermostat fluid. Temperature was controlled manually and measured by a sheathed chromel–alumel thermocouple in the melted tin. For most of the experiments, 20-mgm. samples of azide were weighed into No. 8 blasting caps, the bottoms of which had been rounded on a steel jig to ensure uniform distribution of the charge from sample to sample. A small hole through each cap about 1 cm. from the top permitted the cap to be wired to a holder that could be manipulated in suitable guides from behind a safety screen. In this way, samples could be introduced into the thermostat, or removed from it for quenching in ice-water, in a rapid reproducible manner. Heating times were determined with a stop watch.

B. *Single Crystals*

The behavior of single, large crystals of azide was studied in a furnace made from a short length of 2 mm. bore Pyrex capillary, into one side of which was blown a small hole to admit a platinum–rhodium thermocouple. The electrically heated furnace was mounted in the hole of a microscope stage, the objective lens of the microscope being cooled by a film of water to prevent damage to it. The azide crystal was thrust into the furnace by placing it on a small glass rod ground to semicircular cross section. A thin Pyrex thread fused at one end to the rod acted as a spring under which the crystal could be placed and held securely in position. A micrometer eyepiece in the

microscope permitted crystal dimensions to be measured. As before, heating times were determined with a stop watch.

Materials

Service and dextrin azides were obtained through the courtesy of Canadian Industries Limited. The service material was white, and showed little crystal twinning. The rather fluffy dextrin azide was light yellow, the grains appearing under the microscope as agglomerates.

Large crystals of service azide were made by the method of Miles (13). Many of the crystals so prepared were 3 to 4 mm. long, but were relatively insensitive, not exploding when crushed or broken.

Precision of Measurement

The precision with which the induction period (i.e., time to explosion) could be measured was determined using 20-mgm. samples. For dextrin azide the maximum deviation from the mean value was 5% at 280° C. and 8% at 295° C., while with service azide the deviation rarely exceeded 5% at any temperatures used. Cooling of the thermostat (about 0.5° C.) during the induction period was probably responsible for most of the observed variability, though timing, size of sample, variations in crystal size between samples, and distribution of charge in the tube also contributed to fluctuations in observed induction periods. For example, 10 mgm. dextrin azide in the tube at 295° C. gave an average induction period of 5.4 sec., while with 20-mgm. samples at the same temperature the value was 7.6 sec.

Minimum Explosion Temperature

In blasting caps, a well defined minimum temperature was found to exist, below which explosion of lead azide would not occur, even after prolonged heating, but above which explosion occurred at every trial. For a given batch of azide this minimum temperature was critical within 0.5° to 1° C., but varied as much as 6° C. with different batches of dextrin azide. The value for dextrin azide was generally found to be 270° to 273° C., that for service azide 314° to 315.5° C., when the samples were exploded in the No. 8 blasting caps. It was found, however, that these minimum explosion temperatures could be altered rather drastically by change of the surface:volume ratio of the tube containing the material. For example, with dextrin azide, a minimum explosion temperature of 272° C. in No. 8 blasting caps was increased to 310° to 317° C. in sufficiently small bore glass capillary tubes, while with service azide a change from 314° to 323° C. was readily produced in similar manner.

The minimum explosion temperatures of both types of azide were also found to increase appreciably if the materials were packed by pressure after being introduced into the blasting caps instead of being simply poured into the caps. The increase with dextrin azide was 5° C. while that with service azide was 15° C. with the degree of packing used in the experiments.

The addition of a few drops (approximately 42 mgm.) of dibutyl phthalate to the azide contained in blasting caps also increased the minimum explosion

temperatures over those for untreated materials, the increases noted being approximately 7° and 40° C. for service and dextrin azides respectively. Simultaneously with the marked change in minimum explosion temperature of dextrin azide when treated with dibutyl phthalate there was an increase in the induction period prior to explosion to a value comparable with that for service azide (approximately 86 sec.). In fact, the effect of both packing and wetting with phthalate was generally to make the behavior of dextrin azide resemble more closely that of service azide.

Effect of Temperature on the Induction Period

The effect of temperature on the induction periods of service and dextrin azides in No. 8 caps is given in Table I.

TABLE I

EFFECT OF TEMPERATURE ON INDUCTION PERIODS OF DRY AZIDES

Service azide		Dextrin azide	
Temp., ° C.	Induction period, sec.[1]	Temp., ° C.	Induction period, sec.[1]
320	48.8	277	11.6
325	30.8	280	10.3
335	14.5	285	8.9
345	8.7	305	6.6
355	5.6	325	5.3
365	4.0	345	3.8
375	2.6	365	2.9

[1] *Average of at least four determinations.*

A similar series of experiments was made using azides wetted with dibutyl phthalate. The effect of temperature is then given by the data in Table II.

TABLE II

EFFECT OF TEMPERATURE ON INDUCTION PERIODS OF AZIDES
WETTED WITH DIBUTYL PHTHALATE

Service azide		Dextrin azide	
Temp., ° C.	Induction period, sec.[1]	Temp., ° C.	Induction period, sec.[1]
325	59.8	330	60.2
345	29.4	335	31.0
355	5.8	345	9.0
360	2.8	355	4.0
		365	1.9

[1] *Average of at least four determinations.*

Representing the induction period by t, a plot of log t against $\frac{1}{T}$ gives the curves in Fig. 1.   It will be noted that the relation for service azide is nearly linear when the material is wetted by phthalate and that wetting has again made the behavior of the two types of azide essentially the same.   From the relation

$$\ln t = \frac{E}{RT} + B$$

values of E may be calculated.   For dry dextrin azide the value obtained is 10.6 kcal., while with dry service azide it varies from 31 kcal. at the highest
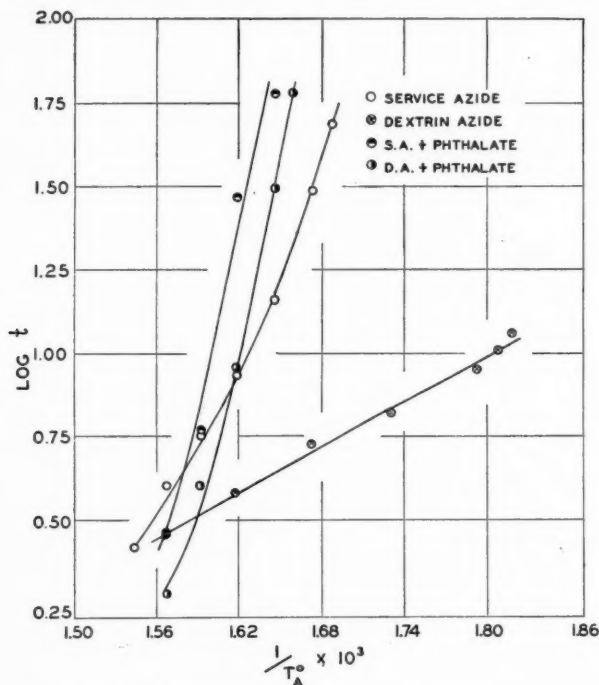

FIG. 1.   *Plot of log $t - \frac{1}{T}$ relations for dry and phthalate wetted azides.*

temperatures used to 65 kcal. at the lowest.   Calculations for the wetted azides, however, give values of 87 and 97 kcal. for service and dextrin azides, respectively, at the lowest temperatures, while at the highest temperatures used the corresponding E values are 66 and 60 kcal.   It is of interest, perhaps, that the values of E for wetted materials do reflect the identical chemical composition of dextrin and service azides, but it is probable that values of E obtained in this way do not represent true activation energies for the reaction leading to explosion, since they are so dependent upon purely physical characteristics of the system.   The reasons for this dependence will become clear later.

Sensitization by Preheating

Service azide is readily sensitized in the Ubbelohde sense (19); that is, if a sample is heated at a given temperature for a fraction of the full induction period, and the pre-explosion reaction quickly quenched, for example, by plunging the container into ice-water, a second heating period culminating in explosion is shorter than the single induction period at that temperature. The extent of sensitization depends on the time and temperature of preheating. Typical sensitization data obtained in the present study are recorded in Table III, where t_1 = preheating time, t_2 = second heating time for explosion, T = temperature during both heating periods, and t = time for explosion by a single heating period at the same temperature. It will be noted that t_2 was

TABLE III

SENSITIZATION OF SERVICE AZIDE

$T = 320°$ C. $t = 47.0$ sec.		$T = 330°$ C. $t = 20.3$ sec.	
t_1, sec.	t_2, sec.	t_1, sec.	t_2, sec.
15	34.8	5	18.3
25	24.8	8	16.4
30	24.8	10	14.6
35	22.8	15	12.3
43	22.2	18	11.7
45	Exploded on withdrawal	19	10.3
		20	Exploded on withdrawal

always less than t by an amount that depended on t_1, and that $(t_1 + t_2)$ was always larger than t. It is of interest that the azide may be preheated to within one or two seconds of explosion, yet require a considerable second heating period, t_2, after quenching to produce explosion. This would suggest that most of the reaction culminating in explosion occurs in a very short time immediately preceding explosion, and that if the rate of the pre-explosion reaction is appreciably influenced by self-catalysis, practically all the catalytic products are produced immediately prior to explosion.

There is a limit to the sensitization possible by preheating. This limit was observed and studied by preheating at temperatures below the minimum explosion temperature so that long preheating periods without explosion were possible. After the preheating treatment, the material was quenched, then brought to explosion at a temperature above the minimum explosion value. The length of the second heating period gives a measure of the degree of sensitization. The data are shown in Table IV, where T_1 = preheating temperature, t_1 = preheating time, T_2 = second heating temperature, and t_2 = second heating time culminating in explosion at T_2.

TABLE IV

SENSITIZATION OF SERVICE AZIDE BY PREHEATING BELOW THE MINIMUM EXPLOSION TEMPERATURE

$T_1 = 310°$ C.　　　　　　　　$T_2 = 320°$ C.

t_1, sec.	20	30	40	50	60	70	80	90	100	120	150
Av. t_2, sec.[1]	38.4	31.4	26.5	23.6	23.6	22.2	21.4	19.9	19.7	18.8	20.3

t_1, sec.	175	200
Av. t_2, sec.[1]	24.4	No explosion

[1] *Average of at least four determinations.*

From the table it is evident that the maximum sensitization corresponded to a reduction in t_2 to about 19 sec. from a normal induction period at 320° C., for a single heating of about 50 sec. Prolonged preheating apparently raised the minimum explosion temperature above 320° C.

Careful re-examination of the sensitization at 320° C. (cf. Table III), with explosion also at 320° C., gave no indication of a limiting sensitization being reached, and the minimum explosion temperature remained essentially unaltered. Hence, material sensitized to the maximum extent without explosion occurring above the minimum explosion temperature would seem to be in a different condition than material whose minimum explosion temperature had been seriously altered by prolonged sensitization below the minimum explosion temperature. Examination of normal, partially sensitized, and fully sensitized azide samples by X-ray diffraction gave no evidence of alteration in the sensitized materials.

No successful sensitization of dry dextrin azide above its minimum explosion temperature was found possible. By preheating slightly below the minimum explosion temperature, the data shown in Table V were obtained. The induction period for a single heating at 280° C. was 9.0 sec. for the batch used. It may be reasonably doubted that the data correspond to true sensitization of the material.

TABLE V

SENSITIZATION OF DRY DEXTRIN AZIDE

$T_1 = 275°$ C.　　　　　　　　$T_2 = 280°$ C.

t_1, sec.	10	7	5	3	3	2	2	1	1
Av. t_2, sec.	No explosion	10.6	10.4	8.0	8.4	8.1	8.1	8.2	8.2

While sensitization of the dextrin material was slight, desensitization was readily accomplished, corresponding to an increase of the minimum explosion temperature from its normal value of 276° C. to a value above 280° C.

Sensitization of dextrin azide was greatly facilitated by wetting with dibutyl phthalate. For a batch that showed, when wetted, an induction period for single heating at 335° C. of 41 sec., it was found that preheating four wetted samples at 335° C. for 25 sec. resulted in explosion on a second heating after 21.0, 17.9, 18.0, and 23.8 sec. for the four samples. Again, wetted dextrin azide behaved similarly to service azide.

Duration of the Sensitization

Duration of sensitization in service azide was studied by preheating four series of samples for 20 sec. at 320° C., and storing them at room temperature under the following conditions.

Series A: In dark, over concentrated sulphuric acid.

Series B: In dark, in nitrogen, over concentrated sulphuric acid.

Series C: In dark, over water.

Series D: Exposed to diffuse light, over water.

Samples were removed periodically and the time of second heating to explosion was measured. The total storage times were 1122 hr. for Series A, 1051 hr. for Series B, 790 hr. for Series C, and 404 hr. for Series D.

. In general, there was considerable variability in the times of second heating to explosion, but with only a few of the samples, among those stored over water, was it impossible to bring about explosion at 320° C. The sensitization effect was essentially unaltered with most of the samples. Those that failed to explode at 320° C. after storage suffered a 6° to 7° C. increase in minimum explosion temperature during storage, to a value of 322° C. This increase in minimum explosion temperature in samples stored over water could be attributed to the fact that, on storage, the azide in such samples tended to bind together, to become lumpy and no longer free-flowing. The data indicated clearly that, over a period of approximately three months, the sensitization was retained essentially unaltered.

A further indication that the sensitization effect was not readily eliminated, even at higher temperatures, was obtained in experiments in which, instead of rapidly quenching the sensitized material in ice-water, it was allowed to cool comparatively slowly. This was done by preheating the samples at 310° C., after which they were raised so that the bottom of the charge container was just above the level of the thermostat fluid for 30 sec., then raised again until the bottom of the container was about 1 in. below the top of the steel heating block, for another 30 sec., then cooled in air for five minutes, during the first minute of which the container was held about 2 in. directly above the block. No ice-water was used to quench the samples. The azide was finally exploded at 320° C. Six samples treated in this way failed to show any significant effect of the rate of cooling on the extent of sensitization by the preheating treatment.

Effect of Phthalate on Sensitized Service Azide

If sensitization of service azide by preheating produces a distinct chemical change in the crystals, it would hardly be expected that wetting sensitized

samples with dibutyl phthalate should obliterate the sensitization. However, when service azide was sensitized to the maximum extent above and below the minimum explosion temperature, then exploded at 335° C. in the presence of added phthalate, the data of Table VI were obtained. Unsensitized samples similarly wetted with phthalate and exploded by a single heating showed an induction period of 37.3 sec. (average) at the same temperature.

TABLE VI

EFFECT OF PHTHALATE ON SENSITIZED
SERVICE AZIDE

Time of sensitization, sec.	Time of second heating, sec.[1]
A. Temperature of sensitization = 310° C.	
100	39.9
120	42.2
150	39.9
B. Temperature of sensitization = 320° C.	
42	40.8

[1] *Average of at least three determinations.*

From previous data, preheating for 120 sec. at 310° C. corresponds to maximum sensitization, while samples heated at 310° C. for 150 sec. should have second heating times longer than those preheated for 120 sec. However, the addition of phthalate has eliminated all the sensitizing effect of preheating, regardless of whether the preheating treatment was above or below that for maximum effect, or whether the sensitization was induced above or below the minimum explosion temperature. The effect of phthalate addition to sensitized service azide would seem to be entirely similar to the effect of adding phthalate to dextrin azide, from which it seems logical to suggest that sensitization of service azide should be explicable on the same basis as the difference in behavior of dextrin and service azides.

Explosion of Mixtures of Service and Dextrin Azides

Since service and dextrin azides differ markedly in their thermal explosion properties, it was of interest to examine the induction periods of mixtures of the two types. Mixtures containing various proportions of the two azides were made and 20-mgm. samples of each mixture exploded at 320° C. The minimum explosion temperature of each mixture was also determined. The results are plotted in Fig. 2.

The data indicate that the properties of the mixtures are sensitive to small changes in the ratios of the components. The plot of t vs. composition is discontinuous at 75% service azide because of an increase in minimum explosion temperature to 321° C. for that composition, while the explosion temperature used throughout was 320° C. The discontinuity would widen
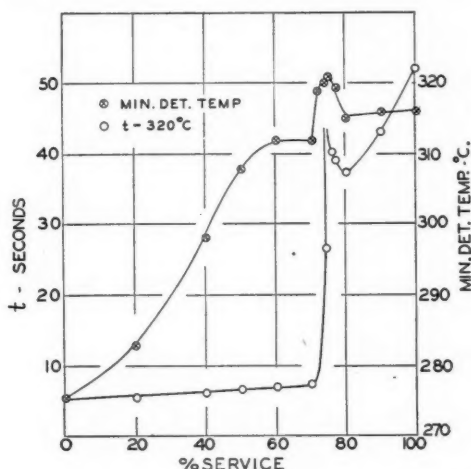

Fig. 2.   *Induction periods and minimum explosion temperatures of service–dextrin azide mixtures.*

at the lower, and disappear for a sufficiently high, temperature of explosion. It is also interesting to note that the discontinuity occurs at percentages of service azide slightly above a range of compositions where the induction periods are closely similar to those of dextrin azide itself, despite the fact that such mixtures may contain as much as 70% service azide.

The effect of temperature on explosion of the various mixtures was also determined. A plot of log t against $\frac{1}{T}$, as in Fig. 3, shows an abrupt change in explosion characteristics of the mixtures at lower temperatures.

The abrupt change in explosion behavior at 75% service azide is accompanied by a maximum in the packing density at the same composition. The relative packing densities of different mixtures were measured by successively weighing 50-mgm. samples of each mixture into a fine bore capillary tube, the tube being tapped and rubbed with a file until three successive measurements of the height of any given sample in the tube gave concordant values. The reciprocal of the relative heights for different mixtures in the same tube gave a measure of the relative packing densities. The data obtained are recorded in Table VII.

It is evident that mixtures of composition in the neighborhood of 75% service azide pack to higher density than mixtures of other compositions.

Explosion of Mixtures of Sensitized and Normal Service Azide

Sensitized service azide resembles dextrin azide in that it has a fairly short induction period. Explosion of mixtures made up of sensitized and normal
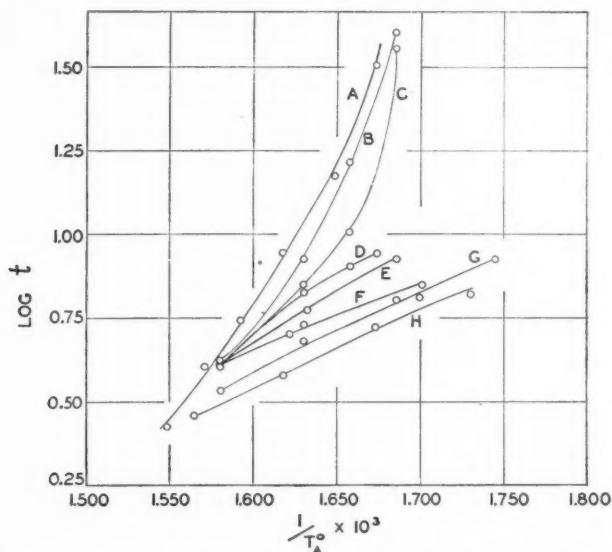

FIG. 3.   *Variation of induction periods with temperature for service–dextrin azide mixtures.*

A = 100% service azide		E = 70% service azide
B = 90% " "		F = 60% " "
C = 80% " "		G = 30% " "
D = 75% " "		H = 100% dextrin azide

service azides should give information on whether the effect of dextrin azide in service–dextrin mixtures is the result of its shorter induction period or of some other factor.

TABLE VII

RELATIVE PACKING DENSITIES OF SERVICE–
DEXTRIN AZIDE MIXTURES

Service azide, %	Height in tube, mm.[1]
0	117.9
70	101.4
75	99.3
80	99.8
100	103.7

[1] *Each value the average of four determinations.*

Service azide was sensitized in 20-mgm. quantities by heating at 320° C. (above minimum explosion temperature) for 25 sec.   Mixtures of this sensitized material with unsensitized service azide were made to various compositions and exploded in 20-mgm. quantities at 320° C.   The minimum explosion temperatures were also determined.   The data, plotted in Fig. 4,
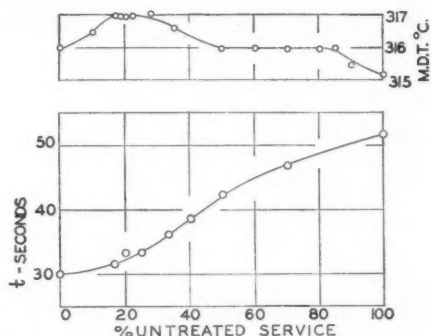

FIG. 4.   *Induction periods and minimum explosion temperatures of mixtures of normal and sensitized service azides at 320° C.*

show a fairly steady increase in induction period with increased content of normal azide, and a slight maximum in the minimum explosion temperature between 20 and 30% content of untreated azide.   At no composition is there any indication of a sharp break in either curve.   It may be inferred then that the unusual curves obtained with service–dextrin azide mixtures are due to factors other than the short induction period of dextrin azide.

From previous experience it was anticipated that the sharp increase in induction period of service–dextrin mixtures in the region of 70 to 80% service azide would be reduced, if not eliminated, by wetting the mixtures with dibutyl phthalate.   Accordingly, 20-mgm. samples of mixtures containing 30, 75, and 80% service azide were wetted with phthalate and exploded at 340° C., the average induction periods being 27.3, 34.2, and 32.3 sec. respectively. Evidently the spread between induction periods for mixtures below and above 70% service azide (cf. Fig. 2) was markedly reduced by wetting with phthalate.

Values of E for Initial and Final Stages of the Induction Period

If, during the induction period, there is first a reaction responsible for sensitization (sensitization reaction) which is fundamentally different from a later reaction culminating in explosion (explosion reaction), it would be expected that values of E for the initial and final stages of the induction period should be significantly different.   The sensitization reaction, for example, might be assumed to form nuclei of some kind which serve to catalyze the explosion reaction.

The value of E for the first part of the induction period (sensitization reaction) was determined by heating service azide for the required times at different temperatures to produce essentially constant degree of sensitization

in the material.   In practice, the temperature and time of sensitization t were adjusted to give an induction period on the second heating of 24 ± 0.5 sec. at 320° C. The data obtained are given in Table VIII. The value of 51 sec.

TABLE VIII

DATA FOR EVALUATING E FOR THE SENSITIZATION
REACTION (SERVICE AZIDE)

Temperature, ° C.	Time of sensitization, sec.
300	100
310	51
320	35
330	20
340	11

at 310° C. is interpolated from Table IV, while the experimentally unattainable value of 11 sec. at 340° C. is estimated from the observations that the induction period for a single heating at 340° C. was 11.5 sec., while preheating up to 10 sec. at 340° C. reduced the second heating period for explosion at 320° C. to 29.2 sec. (from a single heating induction period of 49 sec.).

The data in Table VIII are plotted in Fig. 4, from which a value of E of 37 kcal. was evaluated.

The value of E for the explosion of sensitized azide was also measured. For this estimation, samples were preheated for 20 sec. at 320° C., quenched, then exploded by heating at various temperatures. The data are shown in Table IX.

TABLE IX

DATA FOR EVALUATING E FOR EXPLOSION OF
SENSITIZED SERVICE AZIDE

Explosion temp., ° C.	Time for explosion, sec.[1]
320	29.7
330	16.6
340	8.5
350	5.7
365	3.4
375	2.1

[1] *Each value the average of at least six determinations.*

These data are also plotted in Fig. 5, and yield an E value of 41 kcal.

The values of E for sensitization and explosion agree sufficiently well to suggest that there is no difference between the two reactions.   It would seem improbable, for example, that one reaction (sensitization) produced a catalyst for the other (explosion).

Experiments with Single Crystals

The principal factor governing the minimum explosion temperature of single lead azide crystals was found to be their size, the larger particles exploding at
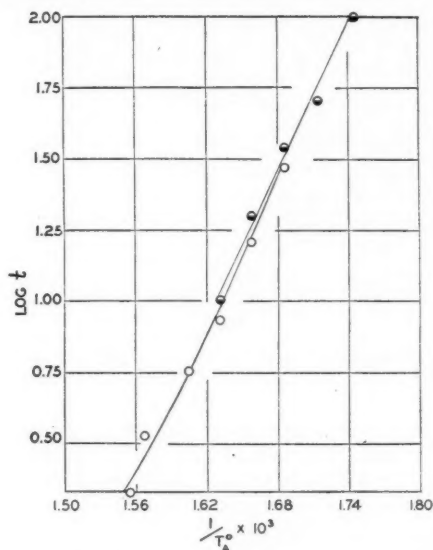

FIG. 5. *Effect of temperature on time of preheating service azide to a given degree of sensitization (upper curve) and on time for explosion of sensitized service azide (lower curve).*

lower temperatures. Some examples of the effect are given in Table X. The dimensions are in divisions of the eyepiece micrometer scale (1 mm. = 65 divisions), and are recorded in order of length, thickness (height), and width

TABLE X

EFFECT OF CRYSTAL SIZE ON MINIMUM EXPLOSION
TEMPERATURE OF SINGLE CRYSTALS

Crystal size, mic. div.	Temp., ° C.	Cross-sectional area, (mic. div.)²	Remarks
43 by 8 by 14	320	112	No explosion
53 by 13 by 10	320	130	" "
53 by 18 by 15	320	270	Broke—25 sec.
44 by 8 by 14	325	112	No explosion
49 by 16 by 16	325	256	Broke—22 sec.
66 by 9 by 14	332	126	No explosion
61 by 18 by 15	332	270	Broke—15 sec.
39 by 9 by 14	340	126	No explosion
50 by 8 by 18	340	144	Broke—17 sec.
52 by 10 by 16	340	160	" —17 sec.
49 by 13 by 17	340	221	" —18 sec.
58 by 8 by 17	347	136	" —13 sec.

of the crystal.   The explosion was incomplete at lower temperatures (below about 350° C.), but the crystal broke up abruptly, accompanied by a faint crackling sound.   The time lag preceding the crystal fracture was taken as the induction period preceding the partial explosion.

It will be noted from Table X that the cross section of the crystal is the important factor in relation to its explosion characteristics.

Activation Energy for Explosion in Single Crystals

A value of E for the explosion of single crystals was obtained by exploding single crystals, of approximately the same size, over a range of temperatures, and timing their induction periods to the nearest second.   The data, given in Table XI, correspond to a value of E of approximately 10 kcal.   This value is much smaller than that for explosion of bulk service azide, but is almost identical with that for dextrin azide.

TABLE XI

EFFECT OF TEMPERATURE ON THE INDUCTION PERIOD
FOR SINGLE CRYSTALS

Temp., ° C.	Crystal size, div.	t, sec.
320	56 by 17 by 20	18
320	59 by 11 by 18	19
334	62 by 15 by 18	16
334	57 by 18 by 20	15
348	61 by 22 by 20	13
348	70 by 20 by 16	12
390	70 by 18 by 23	7
390	70 by 14 by 20	8

Sensitization of Single Crystals

Attempts were made to sensitize single crystals of service azide by pre-heating, the reaction being quenched by quickly withdrawing the crystal from the furnace and cooling it in an air stream.   There was some indication of sensitization, corresponding to a possible reduction of the second heating period from 18 to 16 sec., but reasonable doubt can be entertained of its reality.   After the preheating treatment the crystals showed darkening at the ends and, in more advanced stages of treatment, also along the edges or wherever roughness was visible.   Crystals heated to within one to two seconds of explosion, then quenched, were by no means covered with the dark brown deposit, and on breaking the crystals it was evident that the deposits were on the outer faces only and, at that stage of reaction at least, had not begun to penetrate into the interior.

Self-heating of Single Crystals

With single crystals, it was possible to predict explosion a second or two before it occurred by noting the time at which an apparently abrupt swelling

of the crystal occurred (viewed through a micrometer eyepiece). This swelling was probably a manifestation of self-heating within the crystal. With about 10% of the samples studied, the swelling was reflected in a noticeable increase in length, the magnitude of which was ascertained as approximately 0.6 scale division for a crystal about 60 divisions long. The approximate coefficient of thermal expansion of service azide was estimated by making many measurements of crystal lengths at room temperature and at 310° C. (below the explosion temperature). The crystals were found to expand about 0.4 micrometer division over this temperature range for a crystal length of approximately 60 divisions. If the coefficient of linear expansion is reasonably constant between room temperature and explosion, it is readily estimated that the crystal temperature (as distinct from the furnace temperature) immediately prior to explosion was of the order of 750° C.

Discussion

The results of the present investigation would seem to be adequately explained by merely assuming that self-heating of lead azide, resulting from inefficient dissipation of the heat of decomposition, accelerates the reaction to one of explosive violence. This view is in contrast to others which assume the process to depend on the probability of chains (energy or material) colliding, the probability of simultaneous decomposition of adjacent molecules, or other similar coincidences, to produce sufficiently localized concentrations of energy to bring about explosion. These probability theories are based largely on past observations that the induction periods leading to explosion were variable at constant temperature, whereas the present study indicates that with attention to temperature control, ratio of surface to volume of container, etc., the precision with which the induction periods can be measured is within a reasonable 5% limit.

The present view is also to be contrasted with others which assume the initial formation of catalytic nuclei. The observation recorded earlier that the value of E for the sensitization reaction is essentially the same as that for the explosion of sensitized azide does not suggest that the explosion is catalyzed to any large extent by the products of the sensitization reaction.

The suggestion that the thermal conductivity of the system is a principal factor in the initiation of lead azide seems to provide a ready interpretation of all the observations recorded during the present study. In discussing the behavior under various conditions, clear distinction must be made between temperature of the thermostat and actual temperature within the azide mass and azide crystals.

The lower minimum explosion temperature for dextrin azide, and its shorter induction period, relative to service azide, are accounted for immediately on the plausible assumption that the intercrystal thermal conductivity of service azide is greater than the conductivity between agglomerates in dextrin azide. In such an event, the self-heating in dextrin azide should be more marked than in service azide, and explosion of dextrin azide therefore occurs at a lower

thermostat temperature (but not lower azide temperature), and in shorter time. Similarly, the increase of minimum explosion temperature with increased surface of material in contact with the wall of the sample container may be attributed to greater loss of heat from the sample to the thermostat, so that the thermostat must be maintained at a higher temperature for the explosion temperature to be attained by self-heating within the azide mass. Compression of the charges, which should improve thermal contact between the particles, should, by this argument, also result in increased minimum explosion temperature (thermostat) and such an effect was observed. Likewise, wetting with phthalate, to establish better thermal contact between particles, brought about an anticipated increase in minimum thermostat temperature necessary for explosion. The argument is equally applicable to the behavior of service–dextrin mixtures, where the mixture of maximum packing density, with unquestionably the best thermal conductivity, required the highest thermostat temperature to bring about explosion. Moreover, there is the interesting observation that with such mixtures the induction period is several times that of the sensitive component, dextrin azide, when the proportion of service azide is sufficiently high. This behavior is readily explained on the basis of improved thermal conductivity of the mixtures containing service azide, and is difficult to explain otherwise. Finally, the work on single crystals where larger crystals, with their undoubtedly smaller rate of heat loss, were found to have lower minimum thermostat temperatures for explosion, gives added credibility to the simple concept of self-heating as the main factor in the initiation of azide explosion.

The nature of the sensitization produced by preheating is largely a matter for speculation. However, most of the data obtained in this investigation can be explained by the simple assumption that roughening of the crystal surfaces during preheating may render contact between crystals less intimate, so that heat produced by self-heating is less readily dissipated to the thermostat. The formation of a lead oxide layer, for example, might produce such an effect.

If sensitization resulted from a change in thermal conductivity as suggested it would be expected, and is observed, that samples preheated to within one or two seconds of explosion should require for explosion a second heating period, not of one or two seconds, but sufficiently long to reproduce by self-heating the internal temperature that existed at the time the sample was quenched. Also, the values of E for the preheating and explosion reactions would be expected, and are found, to be similar, since the nature of the reaction involved would presumably remain unaltered. The durability of the sensitization under the various storage conditions used, the failure to sensitize single crystals, and the observed elimination of sensitization in service azide by wetting with phthalate, all receive ready explanation by the assumption that sensitization is due to a surface effect leading to decreased intercrystal thermal conductivity. However, it is not readily apparent on this basis why wetted, but not dry, dextrin azide should be capable of sensitization, nor can more than

a suggestion be offered for the optimum in sensitization reached when samples are preheated below the explosion temperature for prolonged periods. The desensitizing effect of prolonged heating might be due to production of minute fissures in the crystals, thus effectively increasing the surface:volume ratio and increasing the rate of heat loss from the crystals. Such increase in surface: volume ratio should be accompanied by increase in the minimum explosion temperature (on basis of preceding arguments) and such increases, though small, were in fact observed.

With self-heating apparently playing such an important part in the explosion of lead azide it is questionable that the term activation energy should be applied to the quantity E in the expression $\ln t = \dfrac{E}{RT} +$ constant. The value of E has been shown to depend on purely physical characteristics of the system. This dependence, which is readily understood in terms of changes in ease with which the heat of reaction is dissipated, clearly indicates that a value of E so obtained is not a true measure of the activation energy for the chemical reaction culminating in explosion.

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PRELIMINARY OBSERVATIONS OF THE DIELECTRIC CONSTANTS OF VAPORS ADSORBED ON ACTIVATED SILICA[1]

By R. McIntosh,[2] H. S. Johnson,[3] N. Hollies,[3] and L. McLeod[2]

Abstract

A measure of the dielectric constants of several substances adsorbed on silica gel has been obtained by measuring the change in the capacity of an electrical condenser when measured amounts of the substances were adsorbed on silica gel situated between the plates of the condenser. The substances examined were ethyl chloride, n-butane, and ethylene oxide. The plot of capacity change vs. amount adsorbed was found, in all cases, to consist of two or more quite distinct sections, each approximating to linearity. The temperature coefficients of dielectric constant were evaluated. The dielectric constant calculated for adsorbed n-butane was close to that calculated for the bulk liquid, whereas the value calculated for adsorbed ethyl chloride was significantly lower than the value calculated for the liquid.

Introduction

Although adsorption theories, such as those of Brunauer, Emmett, and Teller (4), and Jura and Harkins (10) permit of some inferences concerning the nature of adsorbed layers, relatively few of the physical properties of such layers have been studied in a direct way. The present paper describes attempts to obtain a direct measure of the dielectric constant of the adsorbate by measurement of the change in electrical capacity resulting from increments of vapor to an adsorbent between the plates of an electrical condenser. The relation between the experimentally determined capacity changes and the dielectric constant of the adsorbate is not yet completely established, although the problem has attracted the attention of a number of investigators (2). A slight dependence on the crystal form of the solid component, for example, is indicated. However, a linear relation between the change in capacity on the one hand, and the dielectric constants and volumes of the adsorbate and vapor phase on the other, is often used (1, 8) and appears to give good results. If we indicate the solid, adsorbed, and vapor phases respectively by the subscripts 1, 2, and 3, the fraction of the total condenser volume occupied by each by f_1, f_2, and f_3, the dielectric constant of each by e_1, e_2, and e_3, the relation is (12):

$$e = f_1 e_1 + f_2 e_2 + f_3 e_3 , \qquad (1)$$

where e is the effective dielectric constant of the mixture. An increment of the material being adsorbed produces a change of dielectric constant

$$\triangle e = \triangle f_2 e_2 + \triangle f_3 e_3 , \qquad (2)$$

assuming f_1e_1 to remain unchanged.   Since e_3, the dielectric constant of the vapor, is known, this equation permits the calculation of e_2.   All the uncertainties in the use of this equation do not obscure the fact that a plot of $\triangle e - \triangle f_3 e_3$ vs. amount adsorbed should be very nearly linear if the dielectric constants of successive portions of adsorbate are the same.   In particular, any sharp change of slope in this curve must mean that the two portions of adsorbate corresponding to the two portions of the curve have different dielectric constants.   It may be noted here that values of C quoted subsequently include the small correction $(C_0 \triangle f_3 e_3)$ for changes in the amount of vapor present. C_0 is the capacity of the condenser when empty.

Interpretation of the results of these measurements, though not free from complication, is capable of giving valuable information concerning the physical state and mobility of the adsorbed molecules.   Even more readily detected are *changes* in these properties with the amount adsorbed and with temperature.   For example, if the mobility characteristic of a polar substance in the liquid state were lost in the adsorbed state, the dielectric constant of the adsorbate would show no temperature coefficient.   Measurement of the dielectric constant at different frequencies, moreover, might be expected to establish the 'relaxation time' (5) of the adsorbed molecules.

Previous work of this nature is limited.   Argue and Maass (1) examined the system water–cellulose at one temperature and at a fixed frequency of 500 kc. Higuti (8) examined the system n-propyl alcohol – titanium dioxide gel over an extended temperature and frequency range.   The heterodyne beat method was used in both these investigations.   The present work differs from Higuti's in the technique employed, and in its restriction to a much smaller relative pressure range.   The form of the curves over this limited range is studied in greater detail and with somewhat higher precision.   It is believed that phenomena are revealed here which either did not occur, or were not detected, in the other investigation.   Likewise, still other phenomena, abundantly clear from Higuti's work, do not occur under the conditions of this study.

Our preliminary investigations have been carried out using silica gel and several adsorbates.   The results were obtained by two laboratory groups working in co-operation, at McGill University and at the National Research Council Laboratories, Ottawa.   No extended discussion of the theoretical significance of the results will be attempted until the techniques of measurement and interpretation have been subjected to further test.

Experimental

The measurements consisted of the determination of the amount of vapor adsorbed by the silica gel in the condenser, and the simultaneous measurement of the capacity change resulting from the increment of adsorbate.   A small correction was applied for the increase of capacity due to the free vapor in the cell.   The reversibility of both the adsorption and capacity changes was established by measurement of the capacity decrements on desorption.

The capacity changes were measured by a bridge method, in the one laboratory at a fixed frequency of 3530 c.p.s., and in the other, at several frequencies ranging from 1000 to 60,000 c.p.s. The bridge was adapted for the purpose from a type described by Hartshorn (7). The increase in the capacity of the test condenser was compensated by a decrease in a variable condenser in parallel with it. The 'magnifying' arrangement of condensers described by Hartshorn was used, so that capacity changes of 0.01 $\mu\mu$f. or less could be read on the dial of a precision condenser. The reproducibility of a capacity change varied from $\pm$ 0.01 $\mu\mu$f. at the optimum frequencies (about 10,000 c.p.s.) to $\pm$ 0.2 $\mu\mu$f. at the least favorable frequency (60,000 c.p.s.). Since the changes of capacity for each addition of vapor ranged from 1 $\mu\mu$f. for butane to 5 or 6 $\mu\mu$f. for ethyl chloride and ethylene oxide, the accuracy of the measurements is in the neighborhood of 1 or 2%. This can be improved if the determinations are made at a fixed frequency in the optimum sensitivity range.

Presence of the adsorbate caused only negligible changes in the power factor of the test condenser except in the upper adsorption regions in the case of ethyl chloride. Consequently, if higher frequencies were to be investigated, the heterodyne beat method could be employed.

The dielectric cell finally adopted consisted of three concentric metal cylinders, retained in fixed relative positions by Pyrex glass spacers. In operation the inner and outermost electrodes were kept at ground potential.

The silica gel was a product of the Davison Chemical Corporation. The sieve sizes used in the two laboratories were 40 to 60 mesh and 45 to 80 mesh. The gel was evacuated *in situ* at a temperature of 120° C. under a pressure of 10^{-6} mm. of mercury.

The vapors used were ethyl chloride, *n*-butane, and ethylene oxide, obtained from the Ohio Chemical and Manufacturing Co. The materials were purified by distillation under vacuum from a dry ice – acetone trap to a liquid air trap, the middle fraction being retained.

A standard type of adsorption apparatus, similar to that described by Emmett (6, p. 3 *et seq.*) was used.

Results

When the change in capacity, $\triangle C$, is plotted against the amount adsorbed per gram of adsorbent, V, a plot is obtained that appears to consist of two or more quite distinct sections. Each of these sections approximates to linearity. The slight 'scattering' of experimental points is almost random relative to a straight median line, although a slight tendency toward curvature is noted in some experiments. Two curves for each substance, typical of a larger number of runs, are given in Figs. 1, 2, and 3. The points of discontinuity are approximately located on these plots. In Table I are presented typical values of the ratio of capacity increase to volume increase, $\triangle C / \triangle V$, obtained in successive additions of adsorbate. The results are given only to two significant figures, since the accuracy of the measurements scarcely justifies the retention of the

third figure. This procedure has the advantage of directing attention to the reality of the discontinuities in slope, the feature of greatest importance.

In all cases studied, the discontinuous change of dielectric constant of the adsorbate corresponding to the change in slope of the $\triangle C$ vs. V curve indicates a decrease in this quantity. In other words, the portion of the adsorbate
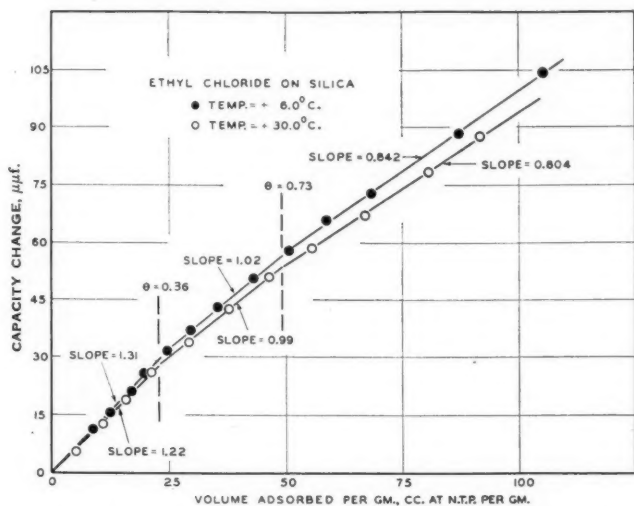

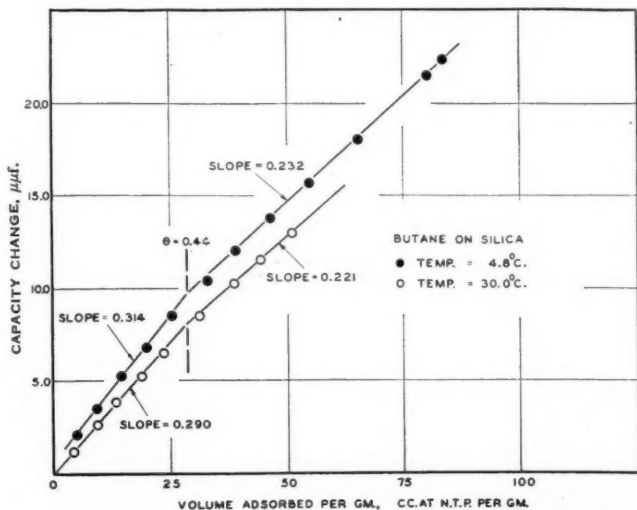FIG. 1. *Effect of adsorbed ethyl chloride on the capacity of a condenser containing silica gel.*

FIG. 2. *Effect of adsorbed butane on the capacity of a condenser containing silica gel.*

corresponding to the second 'linear' region has a lower dielectric constant than the portion corresponding to the first region.   Three such regions were found for ethyl chloride (Fig. 1).   In terms of the amount adsorbed, the two breaks
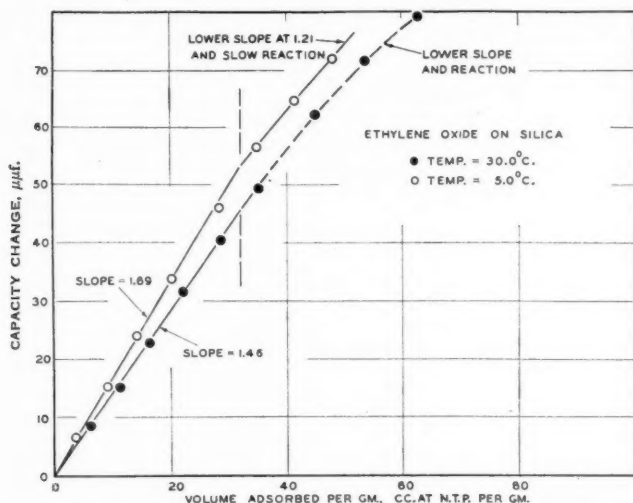

FIG. 3.   *Effect of adsorbed ethylene oxide on the capacity of a condenser containing silica gel.*

in the $\triangle C$ vs. V plots occur at about 23 and 48 cc. of vapor (N.T.P.) per gram of silica gel.   Although it is difficult to locate the break points with high precision, it appears that their positions, expressed in terms of amount adsorbed, do not vary with temperature.

The temperature coefficients of the slopes $\triangle C$ vs. V are very small.   Thus, for an increase of temperature from 6° to 30° C., the slopes of the three sections each decreased about 3 to 6%.   Since this temperature coefficient is much smaller than that which would be expected for liquid ethyl chloride, it was decided to investigate the temperature coefficient for the dielectric constant of n-butane, a typical non-polar substance, under the same conditions.   The apparent temperature coefficient of the adsorbed butane proved to be the same, within the limits of experimental error, as that of the adsorbed ethyl chloride.   This suggests either that the ethyl chloride dipoles are not free to rotate in the field, or that some effect, itself possessed of a temperature coefficient, is operating in such a way as to obscure the normal temperature dependence of dielectric constant for ethyl chloride.   One such possibility is that of association between the adsorbed molecules of ethyl chloride.

From a study of the dielectric constant of the adsorbate over sufficiently wide ranges of temperature and frequency, it might be possible to choose between two such alternatives, particularly if anomalous dispersion were

TABLE I

Adsorption increment, cc. at N.T.P.	Total volume, cc. at N.T.P.	Capacity increment / Volume increment ; $\frac{\mu\mu f.}{cc.\ at\ N.T.P.}$	
Ethyl chloride at 6.0° C.—Frequency, 10,000 c.p.s.			
50.9	50.9	0.23	
19.2	70.1	0.22	
26.5	96.6	0.22	Section I
18.5	115.1	0.22	
27.6	142.7	0.21	
29.2	171.9	0.20	Intermediate
34.9	206.8	0.17	
43.3	250.1	0.17	Section II
44.2	294.3	0.16	
45.2	340	0.15	
56.5	396	0.15	
109.1	505	0.15	Section III
110.2	615	0.15	
Ethylene oxide at 30° C.—Frequency, 10,000 c.p.s.			
33.9	33.9	0.25	
28.9	62.8	0.24	
31.8	94.6	0.25	Section I
33.8	128.4	0.25	
36.4	164.8	0.25	
40.9	205.7	0.21	
57.3	263.0	0.22	Section II
		(Reaction causing appreciable drift)	
Butane at 30.0° C.—Frequency, 10,000 c.p.s.			
23.6	23.6	0.050	
28.1	61.7	0.052	
25.3	87.0	0.050	Section I
27.9	114.9	0.048	
30.5	145.4	0.042	
45.6	191.0	0.042	Section II
41.8	232.8	0.042	

found to occur.   As Table II, showing the dependence of capacity change on frequency, indicates, no anomalous dispersion was found in the frequency range studied, for any of the three adsorbates.

On the assumption of the validity of certain adsorption theories, some inferences can be made respecting the molecularity of the adsorbed layer, the fraction of the surface covered, and so on.   It might be expected that some

TABLE II

EXAMPLES OF THE INDEPENDENCE OF MEASURED CAPACITY CHANGE AND FREQUENCY

Compound	Frequency	Measured capacity change	Temperature, ° C.
Ethyl chloride	1,000	5.83 ± 0.04	30.0
	10,000	5.82 ± 0.01	
	20,000	5.81 ± 0.03	
	40,000	5.74 ± 0.1	
	60,000	6.00 ± 0.2	
Butane	1,000	1.42 ± 0.04	4.8
	10,000	1.42 ± 0.01	
	20,000	1.41 ± 0.03	
	40,000	1.40 ± 0.1	
	60,000	1.40 ± 0.2	
Ethylene oxide	1,000	8.48 ± 0.04	30.0
	10,000	8.42 ± 0.01	
	20,000	8.42 ± 0.03	
	40,000	8.45 ± 0.1	
	60,000	8.34 ± 0.2	

relation between such inferred properties and the form of the $\triangle C$ vs. V curve would be evident. For example, it is possible to calculate the fraction, θ, of the surface covered by adsorbate, utilizing the Brunauer–Emmett–Teller theory as extended by T. L. Hill (9). Thus, if the change in the dielectric constant of the adsorbate were due to regions of differing nature on the adsorbent surface, it might be thought that the breaks in the $\triangle C$ vs. V curves should occur at approximately the same values of θ for different substances. In Table III are given the values of the quantities V_m, C, and θ deduced from

TABLE III

SUMMARY OF ADSORPTION DATA—B.E.T. VALUES

Compound	Temperature, ° C.	Relative pressure range investigated	V_m, cc. at N.T.P./gm.	C	Fraction of surface covered (θ) at breaks
Butane	4.8	0.0−0.4	54.0⎫Multilayer	7.7	0.44
	30.0	0.0−0.3	54.4⎭ formula	6.3	0.44
Ethyl chloride	6.0	0.0−0.6	62.2⎫Multilayer	27.7	0.36, 0.73
	30.0	0.0−0.5	60.7⎭ formula	25.7	0.36, 0.73
Ethylene oxide*	5.0	0.0−0.03	—	—	—
	30.0	0.0−0.09	55.2 Monolayer	348	—

The adsorption data for ethylene oxide are not well represented by either the monolayer or multilayer formula.

the Brunauer–Emmett–Teller adsorption equation.   The first two quantities are defined as follows:

V_m = the volume of vapor (N.T.P.) required to form a monolayer,

C = a quantity related exponentially to the difference in heat of evaporation between the first layer and succeeding layers of adsorbate.

It is evident that no simple correlation exists.

No trend of the dielectric constant of the adsorbate toward that of the bulk liquid is observed in the range studied as the degree of saturation or number of adsorbed layers increases.   This is in contrast to the results of Higuti (8) who, however, worked over a more extended relative pressure range.   These conclusions are based on a comparison of the calculated values for the dielectric constant of the adsorbate with those calculated for the bulk liquids.   The latter were calculated from available data for permanent moments, densities and refractivities using the Onsager equation (11).   Where possible the values so computed were compared with dielectric constant data in the literature.

Preliminary calculations tend to justify the use of Equation (2).   Butane, having no permanent moment, is more likely to have the same value for the dielectric constant in the adsorbed and bulk liquid phases.   The values calculated for the adsorbed film (assuming normal liquid density) at 30° C. are 1.84 for the first, and 1.57 for the second section of the $\triangle C$ vs. V plot. The value calculated for the bulk liquid at 30° C. is 1.77.   Extending this procedure to ethyl chloride, typical data for the first, second, and third sections give values for the dielectric constant of the adsorbate of 5.75, 4.84, and 4.12, respectively at 30° C.   These may be compared with the value of 9.4 calculated for liquid ethyl chloride at the same temperature.

In the study of ethylene oxide it was found that the values of capacity drifted with time toward lower values once an amount of about 40 cc. per gm. of gas had been adsorbed.   This finding suggests that polymerization of the adsorbate was occurring.   From the variation in the rate of drift with temperature, the value of the Arrhenius activation energy was calculated to be 8 kcal. per mole.

Below the apparently critical degree of surface saturation the capacity values were constant, and it is apparent that the temperature coefficient of the dielectric constant for adsorbed ethylene oxide is about 15% for the temperature interval, a value almost identical with that for the computed dielectric constant for the bulk liquid.

A correlation between the slopes of the straight line regions of the $\triangle C$ vs. V plots and the calculated liquid dielectric constants was attempted.   If the slope of these regions is directly related to the dielectric constant of the bulk liquid, then the ratio of slope to dielectric constant should be independent of temperature and have the same value for the various substances.   It is seen from Table IV that these criteria are not met.

TABLE IV

Compound	Dielectric constant of liquid by Onsager formula	Slope of linear sections			Slope of linear sections divided by dielectric constant			Temperature, ° C.
		Section 1	Section 2	Section 3	Section 1	Section 2	Section 3	
Ethyl chloride	9.4	1.22	0.990	0.804	0.130	0.105	0.0856	30.0
Butane	1.77	0.314	0.232	—	0.177	0.131	—	30.0
Ethylene oxide	11.2	1.46	—	—	0.130	—	—	30.0
Ethyl chloride	10.7	1.31	1.02	0.842	0.122	0.0953	0.0786	6.0
Butane	1.81	0.290	0.221	—	0.160	0.122	—	4.8
Ethylene oxide	13.1	1.69	1.21	—	0.129	0.0924	—	5.0

Conclusion

Further experimental data are required before these results can be satisfactorily interpreted. In the meantime, however, our tentative conclusions may be summarized as follows:

(1). The dielectric constants of adsorbed butane and ethyl chloride show the same very small temperature coefficient. Adsorbed ethyl chloride thus behaves like a non-polar compound, owing possibly to restricted mobility, or to a temperature dependent molecular association.

(2). In all cases studied, it appears that the adsorbate consists of two or more portions having different dielectric constants. This is perhaps due to differences in the nature of the adsorption.

(3). The calculated dielectric constant of adsorbed ethyl chloride is significantly lower than that calculated for the bulk liquid. In the absence of direct experimental data for the latter, this discrepancy might also be attributed to restricted mobility or to molecular association.

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APPLICATION DE LA RÉACTION DE MEERWEIN À LA SYNTHÈSE DE DÉRIVÉS DU STILBÈNE ET DU DISTYRYLE[2]

Par Philibert L'Ecuyer[2] et François Turcotte[3]

Résumé

Par la réaction de Meerwein entre l'acide cinnamique et des sels de diazonium convenablement substitués, les o-, m- et p-distyrylbenzènes ont été préparés. La même réaction entre l'acide m-nitrocinnamique et les trois nitranilines a donné naissance aux trois dinitrostilbènes correspondants. D'autre part l'acide cinnaménylacrylique et les sels diazoniums appropriés ont conduit au m-nitro-diphénylbutadiène, à l'o- et au p-méthoxydiphénylbutadiène, ainsi qu'aux m- et p-styryldiphénylbutadiènes. Le p-méthoxydiphénylbutadiène, par réaction de Diels et Alder, a formé un composé d'addition.

Introduction

La réaction de Meerwein (15) entre les sels de diazonium aromatiques et les composés carbonyles possédant une double liaison entre les carbones α et β, présente, lorsqu'appliquée aux acides cinnamiques, un moyen d'accès nouveau à certains dérivés du stilbène (I, R:H) et du distyryle (II, R:H).

Le sel de diazonium préparé, suivant les méthodes ordinaires, en milieu chlorhydrique aqueux, est versé dans une solution du composé carbonyle dans l'acétone, en présence d'acétate de sodium comme tampon et de chlorure cuivrique comme catalyseur. La réaction est accompagnée d'un dégagement gazeux et d'une élévation considérable de température. Il y a avantage à maintenir le mélange réactionnel à la plus basse température qui permette le dégagement gazeux, alors que la réaction de Meerwein domine les réactions secondaires possibles:

a) réaction de type Sandmeyer,

b) déamination par l'acétone (16),

c) formation de résines de nature encore obscure (15),

qui se passent à des températures plus élevées, pour un sel de diazonium donné.

On isole le produit de la réaction par la distillation à la vapeur d'eau et la décantation de la liqueur résiduelle. On extrait ensuite le résidu au benzène, s'il ne se solidifie pas par refroidissement. En tous cas, on lave la solution benzénique ou le résidu à l'ammoniaque et on soumet le produit sec à la distillation sous une pression variant de 0.01 à 0.001 mm. de mercure. La substance ainsi obtenue contient le groupement aryle fixé au carbone α du composé carbonyle de départ.

Depuis sa découverte, en 1939, cette méthode de synthèse fut appliquée avec succès aux acides carbalkoxy-cinnamiques par Fuson et Cooke (11),

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ainsi qu'aux amines halogénées ou alkylées par Bergmann et ses collaborateurs
(4, 5, 6).   Ces derniers introduisirent en outre l'usage de l'acide cinnamén"-
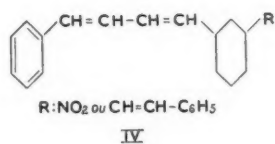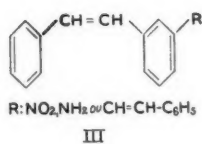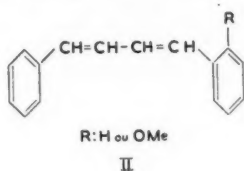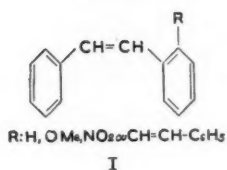acrylique, le vinylogue de l'acide cinnamique.   Bergmann a également
obtenu des résultats favorables avec les sels de diazonium dérivés des
naphtylamines et du p-aminodiphényle (5, 6).

Le but du présent travail fut d'abord la préparation des trois distyryl-
benzènes (I, III, V, R : CH = CH−C₆H₅), en appliquant la méthode de
Meerwein aux sels de diazonium des o-, m- et p-aminostilbènes en conjonction
avec l'acide cinnamique.   Le p-distyrylbenzène avait déjà été préparé par
Kauffmann (13), qui condensa, à cet effet, le chlorure de benzylmagnésium
avec l'aldéhyde téréphtalique, selon la méthode de Grignard, et déshydrata
par pyrolyse le dérivé acétylé du dialcool obtenu.   Récemment Blout et
Eager (8) rapportaient, par une méthode identique comportant l'usage de
l'aldéhyde isophtalique, la synthèse du m-distyrylbenzène.

La condensation des trois aminostilbènes avec l'acide cinnamique s'effectue
avantageusement à des températures inférieures à 20° C. et, comme Bergmann
l'a déjà signalé dans le cas des chloranilines, avec des rendements variant,
suivant la position de substituant styryle sur le noyau aromatique du sel de
diazonium, dans l'ordre ortho < méta < para.   Les résultats que nous avons
obtenus pour le m-nitrostilbène le situent à cet égard entre l'o- et le p-nitro-
stilbène, ce qui confirme une fois de plus cette gradation dans les rendements.
Des trois distyrylbenzènes, l'ortho et le para (I, V, R : CH = CH−C₆H₅)
dont les doubles liaisons sont conjuguées d'une extrémité à l'autre de la
molécule, sont jaunes, tandis que le méta (III, R : CH = CH−C₆H₅) dans
lequel la conjugaison des doubles liaisons s'arrête au noyau central, est incolore.
C'est d'ailleurs ce à quoi on devait s'attendre.

La seconde partie de ce travail avait pour objet d'étudier l'utilisation des
acides cinnamiques substitués à la synthèse de stilbènes avec des groupements
substituants dans les deux anneaux benzéniques.   La réaction de Bischoff (7)
entre les chlorures de nitrobenzyle et la potasse alcoolique ne donne que des
dérivés symétriquement substitués; tandis que la réaction de Perkin ne
convient pas à tous les cas.   Il est maintenant évident qu'en employant,
dans la réaction de Meerwein, des produits de départ convenablement sub-
stitués, on pourra préparer tous les composés prévus par la théorie, symétri-
ques ou non.

A cet effet, nous avons employé comme composé carbonyle α, β non-
saturé l'acide m-nitrocinnamique qui, avec les sels de diazonium obtenus des
o-, m- et p-nitranilines, a donné naissance au 3,2'-dinitrostilbène (VII), au
3,3'-dinitrostilbène (VIII) et au 3,4'-dinitrostilbène (IX).   Cullinane (10)
prétend avoir préparé ce dernier en effectuant la réaction de Perkin entre
l'acide p-nitrophénylacétique et la m-nitrobenzaldéhyde.   Il l'aurait obtenu
de l'acide acétique sous forme de cristaux jaunes de p.f. 155° C. qui exhibent
une fluorescence verte en solution dans l'éthanol ou l'acétone.   Cependant
Harrison et Wood (12) furent incapables de reproduire les résultats de

R: H, OMe, NO₂ ou CH=CH-C₆H₅

I

R: H ou OMe

II

R: NO₂, NH₂ ou CH=CH-C₆H₅

III

R: NO₂ ou CH=CH-C₆H₅

IV

R: NO₂ ou CH=CH-C₆H₅

V

R: OMe ou CH=CH-C₆H₅

VI

VII

VIII

IX

X

XI

XII

XIII
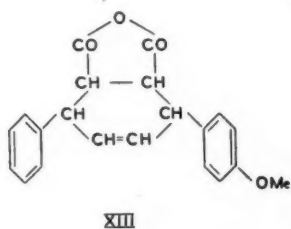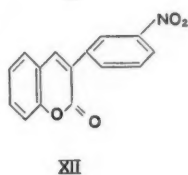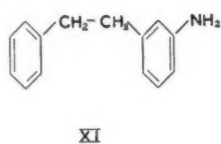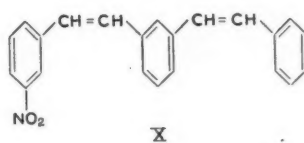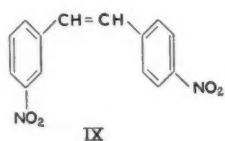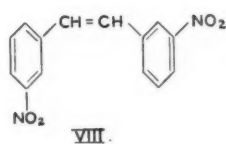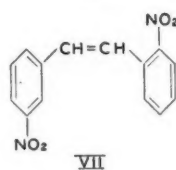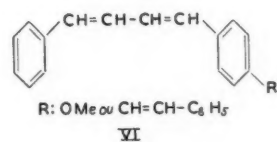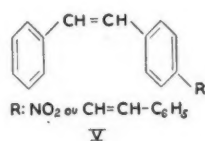
Cullinane, et obtinrent, en opérant dans les mêmes conditions, le dinitro-stilbène (IX) fondant à 217° C., dont les solutions ne manifestent aucune fluorescence. Les propriétés physiques du composé obtenu par la réaction de Meerwein semblent donner raison à ces derniers.

Pour la préparation des dérivés du 1,4-diphénylbutadiène (II, R:H) ou distyryle, la méthode est sensiblement la même que pour celle des dérivés du stilbène. Le composé carbonyle est ici l'acide cinnaménylacrylique ou cinnamalacétique. L'emploi d'une plus grande quantité d'acétone est alors nécessaire pour assurer la complète solubilité de l'acide au moment de l'intro-duction de la solution aqueuse du sel de diazonium. La température de dégagement d'azote est généralement un peu plus élevée et les rendements se comparent assez bien à ceux que l'on obtient avec l'acide cinnamique. Le radical aryle se fixe au carbone α et l'élimination de l'anhydride carbonique est aussi spontanée.

La condensation des sels de diazonium des *m*- et *p*-aminostilbènes a permis la synthèse du 1-(*m*-styrylphényl)-4-phénylbutadiène-1,3 (IV, R : CH = CH$-$C$_6$H$_5$) et du 1-(*p*-styrylphényl)-4-phénylbutadiène-1,3 (VI, R : CH = CH$-$C$_6$H$_5$) respectivement.

Au début de la sublimation de ces deux derniers composés dans un vide de 0.001 mm. de mercure nous avons isolé du stilbène. Nous y voyons l'indice de l'importance relative d'une réaction secondaire prévue, mais non confirmée dans les synthèses précédentes, à savoir l'action réductrice de l'acétone sur les sels de diazonium. En effet, contrairement au stilbène, le nitrobenzène et l'anisole, les produits qui dans les condensations antérieures auraient pu se former grâce à cette réaction secondaire, sont volatils à la vapeur d'eau et sont éliminés durant cette opération. Néanmoins le rendement est satis-faisant dans les deux cas. Encore ici, le composé (VI, R:CH = CH$-$C$_6$H$_5$) complètement conjugué est jaune contrairement à l'autre (IV, R:CH = CH$-$C$_6$H$_5$) qui est incolore.

Deux autres dérivés du distyryle, portant un groupement méthoxyle substitué sur l'un des noyaux, furent préparés par la réaction de Meerwein, en faisant usage de l'*o*- et de la *p*-anisidine successivement, et de l'acide cinnamalacétique: ce sont le 1-(*o*-méthoxyphényl)-4-phénylbutadiène-1,3 (II, R:OMe) et le 1-(*p*-méthoxyphényl)-4-phénylbutadiène-1,3 (VI, R:OMe). Asano et Kameda (1) rapportent la synthèse de ce dernier. Ils l'ont isolé de la fraction insoluble dans la potasse du produit de la réaction de Perkin entre l'aldéhyde *p*-méthoxycinnamique et l'acide phénylacétique.

Enfin, il nous fut loisible de préparer, en solution dans le xylène, suivant la technique de Clar (9), un composé d'addition entre l'anhydride maléique et le composé (VI, R:OMe). Cette réaction se fait avec une extrême simplicité, le produit cristallisant du mélange réactionnel par refroidissement.

Les quelques synthèses que nous venons de citer, ajoutées à d'autres publica-tions relativement peu nombreuses encore (2, 3, 4, 5, 6), permettent d'entrevoir les grandes possibilités de cette condensation de Meerwein entre les sels de

diazonium et les composés carbonyles α, β non-saturés. Les rendements relativement faibles et les difficultés techniques de purification sont, dans plusieurs cas, compensés par l'accès facile des produits de départ et la généralité de l'application de la réaction.

Partie expérimentale

m-Nitrostilbène (*III*, *R* : *NO₂*)

Il a été préparé selon Bergmann (3), mais au lieu de triturer le produit de la réaction, celui-ci est distillé dans le vide. Le *m*-nitrostilbène distille à 160-170° C. (0.05 mm.) sous forme d'un solide jaune. Il cristallise de l'éthanol ou de l'acide acétique en longues aiguilles plates jaune serin de p.f. 112° C. Calculé pour $C_{14}H_{11}O_2N$: C,74.7; H,4.9%. Trouvé: C, 74.8; H, 5.3%.

3,3'-Dinitrostilbène (*VIII*)

Le chlorure de *m*-nitrobenzènediazonium est d'abord préparé par la diazotation de la *m*-nitraniline (13.8 g.; 0.1 mole) dans l'acide chlorhydrique à 25% (50 ml.) et la glace (50 g.) à l'aide d'une solution de nitrite de sodium .(8.4 g.) dans l'eau (20 ml.). La solution du sel de diazonium est alors versée dans une solution froide (0° C.) d'acide *m*-nitrocinnamique (19.3 g.; 0.1 mole) dans l'acétone (600 ml.) contenant de l'acétate de sodium anhydre (20 g.) et du chlorure cuivrique hydraté (4 g.) en suspension. Un dégagement gazeux immédiat se produit à une température maintenue intentionnellement au-dessous de 0° C. et persiste pendant une heure et demie sous une vigoureuse agitation mécanique. La réaction est ensuite complétée en laissant le mélange prendre la température ambiante. Le mélange réactionnel est alors soumis à la distillation à la vapeur d'eau. Après la décantation du liquide chaud surnageant, le résidu brun gommeux se solidifie à froid. Il est pulvérisé, lavé plusieurs fois à l'ammoniaque 2 *N*, puis à l'eau et séché. Le 3,3'-dinitrostilbène se sublime à 175° C. (0.001 mm.). Il est insoluble dans l'éthanol et l'acétone, mais soluble dans le chloroforme et l'acide acétique bouillant. Il cristallise de ce dernier solvant en aiguilles jaune serin de p.f. 240-242° C. Le rendement du produit pur est de 5 g. (18%). Calculé pour $C_{14}H_{10}O_4N_2$: N, 10.3%. Trouvé: N, 9.9%.

3,2'-Dinitrostilbène (*VII*)

La réaction de Meerwein est effectuée comme précédemment à partir de 0.1 mole d'*o*-nitraniline et de 0.1 mole d'acide *m*-nitrocinnamique. Favorisé par une agitation mécanique énergique, le dégagement gazeux commence vers 8° C. et persiste pendant une heure et demie. Le 3,2'-dinitrostilbène se sublime à 160° C. (0.001 mm.). Il cristallise de l'alcool éthylique en aiguilles jaune orange de p.f. 150° C. Le rendement du produit pur est de 3.5 g. (12%). Calculé pour $C_{14}H_{10}O_4N_2$: N, 10.3%. Trouvé: N, 10.0%.

3,4'-Dinitrostilbène (*IX*)

La réaction de Meerwein est exécutée de la même façon à partir de la *p*-nitraniline (0.1 mole) et de l'acide *m*-nitrocinnamique (0.1 mole). Le

dégagement gazeux se produit vers 12° C. et persiste pendant une heure. Du résidu sec de la réaction le 3,4-dinitrostilbène se sublime à 170° C. (0.001 mm.).   C'est un solide insoluble dans l'éthanol qui cristallise de l'acide acétique en aiguilles jaune citron de p.f. 220-222° C.   Le rendement du produit pur est de 7 g. (25%).   Calculé pour $C_{14}H_{10}O_4N_2$: N, 10.3%.   Trouvé: N, 10.2%.

o-Distyrylbenzène $(I, R : CH = CH-C_6H_5)$

L'o-aminostilbène (14 g.; 0.07 mole) dans l'acide chlorhydrique à 25% (30 ml.) et la glace (30 g.) est diazoté par l'addition d'une solution de nitrite de sodium (5.2 g.) dans l'eau (10 ml.).   La solution du sel de diazonium est versée dans un mélange refroidi (0° C.) d'acide cinnamique (10.6 g.; 0.07 mole), d'acétone (100 ml.), d'acétate anhydre de sodium et de chlorure cuivrique hydraté (3.2 g.).   Le dégagement gazeux se passe à 20° C. et dure une heure et demie.   L'o-distyrylbenzène est isolé de la même façon que dans le cas du m-nitrostilbène.   Il se sublime à 130-140°C. (0.001 mm.).   Il cristallise de l'alcool éthylique en aiguilles jaunes de p.f. 120-122° C.   Rendement du produit pur: 3 g. (15%).

m-Distyrylbenzène $(III, R : CH = CH-C_6H_5)$

La diazotation du m-aminostilbène et la réaction avec l'acide cinnamique sont réalisées exactement comme dans le cas précédent.   Le dégagement gazeux se produit vers 12° C. et dure trois heures.   Le m-distyrylbenzène se sublime entre 170-180° C. (0.001 mm.).   Il est soluble dans l'éthanol et l'isopropanol à chaud, dans le benzène, le toluène et le chloroforme à froid. De l'acide acétique il cristallise en lamelles blanches de p.f. 182° C.   Rendement du produit pur: 4 g. (20%).   Calculé pour $C_{22}H_{18}$: C, 93.6; H, 6.4%. Trouvé: C, 93.3; H, 6.5%.

p-Distyrylbenzène $(V, R : CH = CH-C_6H_5)$

La réaction de Meerwein entre le p-aminostilbène et l'acide cinnamique est effectuée avec les mêmes quantités de substance et de la même façon que pour les autres distyrylbenzènes.   Le dégagement gazeux se fait vers 25° C. et est terminé après deux heures d'agitation.   Le p-distyrylbenzène se sublime à 150-160° C. (0.0005 mm.).   C'est un solide insoluble dans la plupart des solvants organiques, mais soluble dans le chloroforme et le xylène. Il cristallise de ce dernier en aiguilles jaunes de p.f. 266° C.   Le rendement du produit pur est de 7 g. (35%).   Calculé pour $C_{22}H_{18}$: C, 93.6; H, 6.4%. Trouvé: C, 93.2; H, 6.5%.

3-(m-Nitrophényl)-coumarine (XII)

La solution du sel de diazonium préparé à partir de la m-nitraniline (34.5 g.; 0.25 mole) est versée dans une solution à 0° C. de coumarine (37 g.; 0.25 mole) dans l'acétone (200 ml.) contenant en suspension de l'acétate anhydre de sodium (50 g.) et du chlorure cuivrique hydraté (5 g.).   Le dégagement gazeux se produit au-dessous de 20° C. et est terminé en moins d'une heure d'agitation.   Le mélange réactionnel est traité comme auparavant et le résidu

est trituré avec de l'éther (100 ml.), filtré, cristallisé trois fois de la pyridine, puis de l'acide acétique. La 3-(*m*-nitrophényl)-coumarine se sépare sous forme de cristaux blancs de p.f. 260-261°C. Calculé pour $C_{15}H_9O_4N$: N, 5.3%. Trouvé: N, 5.4%.

1-(*m-Nitrophényl*)-4-phénylbutadiène-1,3 (*IV, R : CH = CH − C₆H₅*)

Il a été préparé selon la méthode de Bergmann (3). Le solide brun obtenu en suivant la méthode d'isolation employée pour le 3,3′-dinitrostilbène est soumis à la sublimation dans le vide. Le 1-(*m*-nitrophényl)-4-phénylbuta-diène-1,3 se dépose entre 160-180° C. (0.005 mm.). C'est un solide jaune qui cristallise de l'acide acétique. P.f. 145° C. Rendement de la substance pure: 3 g. (12%). Calculé pour $C_{16}H_{13}O_2N$: C, 76.5; H, 5.2%. Trouvé: C, 76.3; H, 5.5%.

1-(*o-Méthoxyphényl*)-4-phénylbutadiène-1,3 (*II, R:OMe*)

Le chlorure d'*o*-méthoxybenzènediazonium est préparé par la diazotation de l'*o*-anisidine (24.8 g.; 0.2 mole) dans l'acide chlorhydrique à 25% (50 ml.) et la glace (50 g.). Sa solution est ensuite versée dans un mélange froid (0° C.) d'acide cinnamalacétique (33.2 g.; 0.2 mole), d'acétate de sodium anhydre (40 g.), de chlorure cuivrique hydraté (8 g.) et d'acétone (600 ml.). Le dégagement gazeux se produit entre 10 et 15° C. et se continue pendant une heure. Le résidu de la réaction isolé de la façon ordinaire est distillé dans le vide. Le 1-(*o*-méthoxyphényl)-4-phénylbutadiène-1,3 distille entre 120-130° C. (0.01 mm.) sous la forme d'une huile qui, additionnée d'un peu d'éthanol dilué, se solidifie par refroidissement dans un mélange de glace sèche et d'acétone. Après cinq cristallisations de l'alcool éthylique dilué il apparaît sous forme d'aiguilles blanches de p.f. 74° C. Rendement: 7 g. (18%). Calculé pour $C_{17}H_{16}O$: C, 86.4; H, 6.8%. Trouvé: C, 86.1; H, 6.9%.

1-(*p-Méthoxyphényl*)-4-phénylbutadiène-1,3 (*VI, R : OMe*)

La réaction de Meerwein est exécutée à partir des mêmes quantités de *p*-anisidine et d'acide cinnamalacétique et de la même façon que dans le cas précédent. Le dégagement gazeux se passe entre 12 et 15° C. et est terminé après une heure d'agitation. Le 1-(*p*-méthoxyphényl)-4-phényl-butadiène-1,3 se sublime à 175° C. (0.01 mm.). Il est insoluble à froid dans l'alcool éthylique. De l'acide acétique il cristallise en aiguilles blanches de p.f. 162° C. Rendement du produit pur: 10 g. (22%). Calculé pour $C_{17}H_{16}O$: C, 86.4; H, 6.8%. Trouvé: C, 86.3; H, 6.9%.

Composé d'addition (XIII)

Un mélange de 1-(*p*-méthoxyphényl)-phénylbutadiène-1,3 (2 g.) et d'an-hydride maléique (15 g.) dans le xylène (20 ml.) est maintenu à l'ébullition pendant environ 25 min. Il en résulte une solution claire dont le composé d'addition se sépare, par refroidissement, en aiguilles soyeuses blanches qui cristallisent de l'acide acétique. P.f. 193° C. Le rendement est quantitatif. Calculé pour $C_{21}H_{18}O_4$: C, 75.4; H, 5.4%. Trouvé: C, 75.1; H, 5.5%.

1-(p-Styrylphényl)-4-phénylbutadiène-1,3 (VI, $R : CH = CH - C_6H_5$)

La condensation de Meerwein est effectuée entre le sel de diazonium préparé à partir du *p*-aminostilbène (6 g.; 0.03 mole) et l'acide cinnamalacétique (5.5 g.; 0.03 mole). Le dégagement gazeux apparaît entre 20 et 25° C. et persiste pendant une heure et demie d'agitation mécanique continue. Le résidu de la réaction se sublime vers 175-180° C. (0.001 mm.). Le 1-(*p*-styryl-phényl)-4-phénylbutadiène-1,3 cristallise de l'acide acétique en lamelles jaunes de p.f. 254-255° C. Rendement: 2.5 g. (25%). Calculé pour $C_{24}H_{20}$: C, 93.5; H, 6.5%. Trouvé: C, 93.2; H, 6.7%.

1-(m-Styrylphényl)-4-phénylbutadiène-1,3 (IV, $R : CH = CH - C_6H_5$)

Le *m*-aminostilbène (6 g.; 0.03 mole) dans l'acide chlorhydrique à 25% (20 ml.) additionné de glace (30 g.) est diazoté sous l'action d'une solution de nitrite de sodium (2 g.) dans l'eau (5 ml.). La liqueur diazotée est ensuite versée dans une suspension froide (0° C.) d'acétate de sodium anhydre (8 g.) et de chlorure cuivrique hydraté (1.5 g.) dans une solution d'acide cinna-ménylacrylique (5.5 g.; 0.03 mole) dans l'acétone (150 ml.). Le mélange réactionnel est plongé dans un bain d'eau tiède et vers 20° C. il apparaît un dégagement gazeux qui dure pendant une heure et demie d'agitation mécani-que. Le produit de la réaction est alors soumis au traitement habituel et le résidu est sublimé dans le vide. Le 1-(*m*-styrylphényl)-4-phénylbutadiène-1,3 se présente alors entre 150-160° C. (0.003 mm.). C'est un solide blanc insoluble à froid dans l'éthanol, soluble dans le benzène, le chloroforme et la pyridine. Il cristallise de l'acide acétique. P.f. 159° C. Calculé pour $C_{24}H_{20}$: C, 93.5; H, 6.5%. Trouvé: C, 93.3; H, 6.6%.

Remerciement

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The Preparation of 1,10-Phenanthroline
From o-Phenylenediamine

The preparation of 1,10-phenanthroline from o-phenylenediamine was carried out by Blau (1), with a reported yield of 30%, but the experimental details were not recorded, and his work has not been duplicated. Hieber and Mühlbauer (2) reported an 18% yield by this synthesis. Smith and Richter (4, 6), and Smith (5) have reported this method of preparation of 1,10-phenanthroline to be unsuccessful, and they state that the desired reactions are accompanied by so many side reactions that the isolation of the pure base is very difficult. We have found that if the method of Hieber and Mühlbauer is followed closely, a yield of nearly 20% of the base may be obtained.

EXPERIMENTAL

o-Phenylenediamine (30 gm.), dry glycerol (165 gm.), and arsenic pentoxide (78.9 gm.) were mixed well, and concentrated sulphuric acid (sp. gr. 1.84, 150 gm.) was added. The resultant mixture was dark red and quite fluid. The mixture was heated, using an oil bath, until it began to reflux, after which the temperature of the reaction mixture was maintained just high enough to cause very gentle refluxing. The bath temperature was held to a maximum of 10° C. above the reaction mixture temperature. The mixture was refluxed for 15 hr., then diluted with three times its volume of warm water. The mixture was filtered and the filtrate was carefully neutralized to litmus with 10 N sodium hydroxide, then acidified with 4 ml. of 3 N sulphuric acid. The black tarry precipitate formed was filtered off and extracted with 330 ml. of hot 3 N sulphuric acid. To the extract plus the filtrate was added a solution of 90 gm. mercuric chloride in 700 ml. hot water. The fine brown precipitate that formed was allowed to settle and was filtered off. The filtrate was green.

The precipitate was decomposed by suspending it in 700 ml. hot water and saturating the hot mixture with hydrogen sulphide. The mercuric sulphide formed was filtered off, and the filtrate made alkaline with 40 ml. of 10 N sodium hydroxide, a black tarry suspension being formed. The mixture was evaporated on the water bath as far as possible, and the solid dried for one hour at 130° C. The dry residue was distilled under 3 mm. pressure, a yellow oil distilling over between 150° and 190° C. On recrystallizing the solidified product from water, 9.7 gm. of 1,10-phenanthroline monohydrate, m.p. 103° to 103.5° C., was obtained. This is a yield of 17.6%.

The above procedure was repeated four times by two different workers, in two cases with a reflux time of eight hours, and the yields obtained averaged 11 gm. (20%).

An attempt to modify the reaction using boric acid reduced the yield to 1%. Use of the acetylated amine, as suggested by Manske et al. (3), gave a 0.7% yield, while a reduction in the amount of sulphuric acid to 99 gm. lowered the yield to 2.7%. The critical feature of the reaction is apparently the temperature of refluxing; if this is allowed to rise even slightly for a short time, there

is practically no yield. The time of reflux did not seem to affect the yield appreciably, and the eight hour period may be longer than necessary; Hieber and Mühlbauer (2) record two to three hours.

The green filtrate obtained when the mercury salt of 1,10-phenanthroline was filtered off contained an unidentified by-product, which behaved as an acid–base indicator, turning purple above pH 5.5 and green below pH 4.7.

We wish to acknowledge the assistance of Messrs. D. Aziz, E. C. Gain, and D. M. Steiner with the experimental work.

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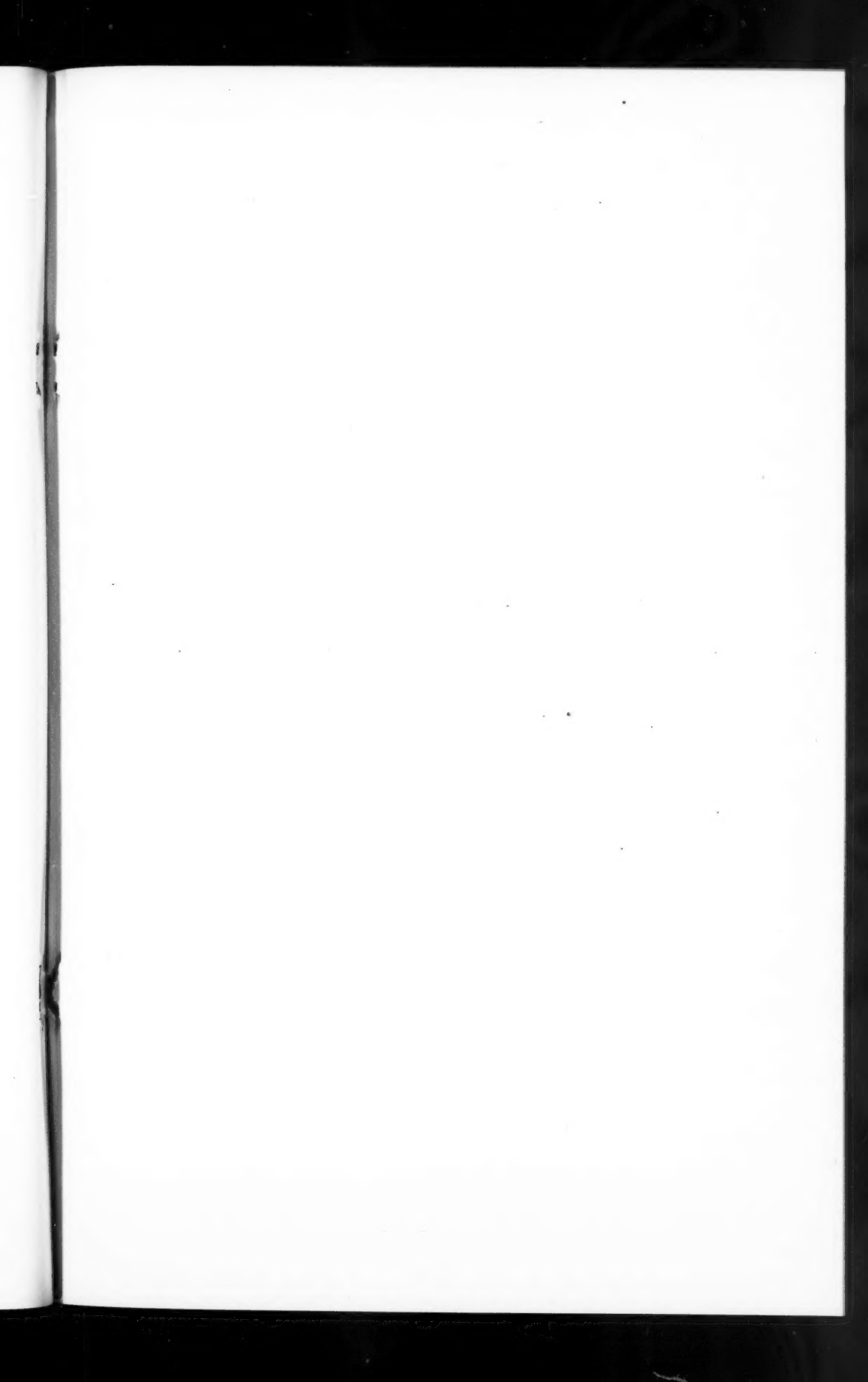
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ABSTRACT:—**An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.**

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